

**PROCEEDINGS
NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE
ON STANDARDIZATION OF
CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS**

**METAIRIE, LOUISIANA
MAY 14-15, 1992**

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FINAL REPORT

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Standardization of Carbon-Phenolic Materials and Processes

Volume 1, Experimental Studies

Volume II, Test Methods and Specifications

Standardization of the Carbon-Phenolic Test Methods and Specifications

Proceedings, Laguna Hills, California, May 1988

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Proceedings, Metairie, Louisiana, May 1992

**SPIP - NOZZLE INITIATIVE ADVISORY COMMITTEE ON
CARBON PHENOLIC CONSTITUENT
AND COMPOSITE TEST METHODOLOGY
9th Biannual Meeting**

Howard Johnson Conference Center
Metairie, Louisiana

**AGENDA
Thursday, May 14, 1992**

- 8:30 AM - 8:35 AM Introduction by Committee Chairman Bill Hall,
Mississippi State Univ. and COTR - Cindy Upton,
NASA/MSFC
- 8:35 AM - 8:50 AM NASA Video Tape Library
- Cindy Upton, NASA/MSFC
- 8:50 AM - 9:00 AM Product Code Identification
- Keith Hill, Hercules
- 9:00 AM - 10:00 AM NMR Progress
- Tom Fisher, Miss. State
- Roman Loza, BP/Hitco
- 10:00 AM - 10:30 AM IR and DMTA Workshop
- Roman Loza, BP/Hitco
- 10:30 AM - 10:45 AM HPLC Test Methods
- Cindy Upton, NASA/MSFC
- 10:45 AM - 11:00 AM Aerospace Database Update
- Ken Drake, Aerospace
- 11:00 AM - 12:00 PM M Vision Database Demonstration
- Kurt Loomis, PDA Engineering
- 12:00 PM - 1:00 PM Lunch
- 1:00 PM - 3:00 PM Constituent Fingerprinting (Martin Marietta Corp.)
- Laurie Rando, Overview
- Frank Stone, Chemometrics
- 3:00 PM - 4:00 PM Cured Materials Test Development
- Eric Stokes, SoRI
- 4:00 PM - 5:00 PM Engineering Needs for Computer Modeling
- Bob Bunker, Thiokol
- Greg Crose, PDA

THE INDUSTRY ADVISORY COMMITTEE

FOR

CARBON - PHENOLIC CONSTITUENT TEST METHODOLOGY

IS

CONSTITUTED UNDER PROJECT 3:2.1.1

OF THE

SOLID PROPULSION INTEGRITY PROGRAM

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**AGENDA
Friday, May 15, 1992**

- 8:30 AM Leave from hotel lobby to NASA, Michoud Facility
- 9:00 AM - 11:30 AM Tour NASA Michoud space shuttle external tank and ASRM
nozzle ablative component manufacturing facility.
Review action items from Wednesday and Thursday meetings.
- 11:30 AM - 12:00 PM Return to Conference Center
- 12:00 PM - 1:00 PM Lunch at Conference Center

**SSIP - NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE
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**HOWARD JOHNSON CONFERENCE CENTER
METAIRIE, LOUISIANA
MAY 14-15, 1992**

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**PROCEEDINGS
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ON STANDARDIZATION OF
CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS**

HELD AT

**METAIRIE, LOUSIANA
MAY 14-15, 1992**

COMPILED BY

EXECUTIVE COMMITTEE

**WILLIAM HALL
MISSISSIPPI STATE UNIVERSITY**

**PAT PINOLI
LOCKHEED RESEARCH AND DEVELOPMENT DIVISION**

**CINDY UPTON
NASA - MARSHALL SPACE FLIGHT CENTER**

**TONY DAY
THIOKOL CORPORATION**

**KEITH HILL
HERCULES**

Hall The SPIP program, the Solid Propulsion Integrity Program, the overall charter for the program is on the viewgraph. The program has several subtasks. We are funded and operated out of Task 3 which is nozzle technology and out of the Task 3, we are Subtask 3.1.1.1 and 3.2.1.1. The 3.1.1.1 is the cured material and the 3.2.1.1 is the constituent material. We have a handout that reviews the past eight biannual meetings that we have had and where the committee stands at this time in our charter work. Our approach to meet the objectives of the SPIP charter and our subtasks goals, this industry advisory committee has an executive committee that meets at least once a week, either in person or by telephone. The executive committee is composed of Tony Day from Thiokol, the Huntsville Space Operations; Keith Hill from Hercules; Pat Pinoli from Lockheed; Cindy Upton, our NASA committee member; and I am Bill Hall from Mississippi State University.

This is our materials flow chart at the present time. Yesterday we had an ASRM update and eventually we will switch over to the ASRM, but as of today this is the materials flow chart for the RSRM that we operate under. All the suppliers and processors are shown there that are qualified as of today.

Does anybody have any questions about why we are here and what we hope to accomplish? The moderator today is going to be our NASA representative, Cindy Upton, and she will proceed from here.

Upton

The first item on my agenda is supposed to be about a video tape library, but this has to do with a broader aspect subject, documentation in general. This group puts out so much information which is to be made available to the solid rocket motor community as a whole, that we are getting a little bit behind in formatting it. This came to my attention back in the winter when we were thinking about putting JANNAF standards and we looked into what it take to make a JANNAF standard and it quite formidable, to say the least. We would have to take all the testing procedures that we have done up to this point and do a series of round robin tests. That did not seem practical for what we wanted to do, so instead the executive committee started thinking about it, and we decided it would be a really good idea to come up with a SPIP standard from this group. Basically it would be a compilation of tests that this group has blessed through round robins or through any other kind of extensive testing to prove the efficiency and effectiveness of a certain tests. Also if we had two similar, but different, tests, we could include them both in our document. Right along with that, we were thinking in terms, if any of you are familiar with JANNAF, you know that the CPIA group puts out documents for each specific section. We could have SPIP standards on cured materials testing, SPIP standards on carbon testing, and however we decided to divide it out. Primarily in the areas of the testing that we have got that could be done by multi-testing sites, we were thinking about a video tape library. This would be controlled by our group and distributed by our group and it would be just an education tool for someone not familiar with the test, but

for someone who wanted to compare how they do a specific test compared to how someone else does a specific test, to look at it and discern the differences themselves. We have not done a lot of thinking or planning on this. It is just an idea that came up that we thought was a good one. We have gotten a lot of support for it at NASA. It is something that really hasn't been done before, so we feel that we would be pretty much on the vanguard of putting our group's work in a good format. We were thinking that you would have a hard copy of the test plan, but you would have the video tape with the person doing the steps right along with it. We haven't done a great deal of planning. We don't really know exactly which tests we will put in on this, but leading up to this, we are also thinking about the best way to improve cured materials. I don't have a lot of travel money. I can't go around to all the testing sites. I am not very familiar with cured materials testing because I am not a mechanical engineer. If we had some sort of tape that we could all view and compare different testing capabilities, it would make a lot more sense to me. We are working on cured materials with Eric Stokes at SORI, who will be giving a presentation on it later, but video tapes are very expensive once you get into really glossy, slick productions. We were thinking that we would just have an on-site home movie kind of a thing. Everybody has a camcorder. What we would do is we would just ask everyone to document the test method being considered. For instance, in the area of cured materials testing, some of you have given me your surveys back. When we start looking at, maybe different ways to do a double notch shear

test, we would want to see our Aerojet does it, how Hercules does it and how Thiokol does it. What I need from you, I guess the action item is, before the meeting is over, would a representative from each testing agency, please identify a representative with whom I can work to set up this video tape library. That is all I wanted to say about that and to tell you that I do feel that we need to start compiling what we have got going here. What I call the "living document" is constantly changing. It needs updating right now and I just updated it in March. This is a good working document. The next thing that I want to do with this document is to expand some of the bullets so that they are more explanatory so that any committee member can refer to this document to get specific information on our committee for use in their own presentations to their own management and their own working group. I will be updating that copy for you by November.

Croese Has this committee considered a military handbook as a way of dissemination of information, storage and archiving, and so on?

Upton I know that military handbooks have been looked into. We are not quite sure to what level of involvement we want to get into. Right now we just want to make everything available to the government agencies who should be aware of our work. The final format has not been decided. We don't have budget for this. This will be something that the executive committee is putting together.

Crose In the 3.1 task area, we looked into the other kinds of testing and what we would do with the data and so on and so forth, and we came to the conclusion that a military handbook project would be an appropriate way to proceed. We put together a report on that subject and some presentations and at a later date, maybe I could go through that for this committee. We established communication with the people in Washington about doing that and they are very interested. When we did pitch it, we did include this committee, the product of this committee as a part of that. Let's at least put in the back of our minds that this is something that we might proceed with or pursue or to encourage.

Upton I do want feedback on what format would be best for our particular group. Would you mind maybe presenting yours to the executive committee between now and November so that we can start working on this.

Crose Just call me and I can arrange it. I can send you the reports that we made.

Thomas Greg, does that carry a mil handbook number?

Crose Well, it doesn't now because it is not an official project.

Thomas No, but I mean eventually.

Croese It would, yes.

Thomas Wouldn't it make more sense to publish it under a NASA report number?

Croese The government mechanism is in place for a military handbook and what I have heard is that it would get further that way.

Upton As a military handbook?

Croese As a military handbook, as opposed to a NASA publication.

Upton What do you mean, "it would get further"? Further disseminated into community?

Croese It would be more permanent and more open and available to a broader community. There is more emphasis on military handbooks than there is on a corresponding thing from NASA.

Upton We definitely want to weigh all the possibilities, so we would want to look at it both as a NASA report and as, I guess, a military handbook.

Croese The idea is to get the military involved in some fashion.

Upton Right.

Croese It would be necessary, for example, to have a military sponsor.

Upton Well, we have the Air Force represented here. Quite frankly, though, we have had problems in finding representatives in other branches of service that wanted to support our group. Part of the problem trying to go through the JANNAF was that we would have had to stop work in progress to go back and put it in a format, just to meet JANNAF's needs and we wouldn't be furthering our own charter. That is my biggest concern with a military handbook. I would still like to hear what our responsibilities would be for us to support that.

Basically, all I need is to get started, but I would like to set up these home movies. We have a lot of tests that we do need to optimize and get out to the industry for everyone's use. In my case, for ASRM, they are in pretty desperate need of some testing that is in place right now. I would appreciate it if some representatives could be identified to me for this purpose. This would just be the preliminary work. Nothing slick and glossy, you just basically tape the test in progress.

The next thing on our agenda is a close out of our Task 8 which was product code identification. Keith Hill is going to talk a little bit about this. This had

been on our agenda for quite some time and at the November meeting we announced that we wanted to close it out and move ahead. We basically heard from different sides and chose something in the middle that we felt was generic enough to serve our purposes, but would do the job. Keith, if you would come up here and present our findings.

Hill

You will notice that the handout is probably the shortest handout of the whole meeting. As Cindy mentioned, we have been talking about this and I first became aware of this, of course, in Sacramento, when I attended my first advisory committee meeting. The subject was called product code identification and I heard quite a discussion, back and forth, about the pros and cons. There were a lot of cons about this product code identification. It seemed like we were talking about a 12 digit code, or some other large number of digits that would identify a material and that seemed to be opening a lot of, a large can of worms. The result of that, we thought a little bit about what we could do to really answer these concerns we have, the need for pedigree, the need for identification, and the need for traceability. It is interesting that under this traceability issue, we fired at Hercules just within the last two or three weeks, the oldest T4 motor that we had ever fired. The question comes up, "Well, what if there is a need to go back and trace the properties of the, trace the material that were in that motor?". With, I guess you would call it a system, that we are currently using, there are some problems with material control. These were talked about pretty well last

time. I didn't want to get into a big discussion on those problems. I would like to present what I have given as a handout as a middle of the road solution. What we are calling it is a Prepreg Material Identification Sheet and if we look at these things item by item, for instance, this would be something like FM 5055. This would be filled out under each of these items. We have prepreg, filler, converter, and the fiber. By the way there is typo on this one. You don't need this one because converter is filled in right there. This is the type of information and the thinking on the committee was that once we identify FM 5055, then we have this sheet filled out accordingly and then if something happens wherein one of these items changes, then we should have new designation. It is not 5055 anymore, but maybe FM 5056, or whatever would be chosen. So there is not the confusion that, well, if I say FM 5055, who knows what is in it.

Beckley Keith, we have been through it before, but you do get a letter suffix change if there is a change. That is the policy.

Thomas The certification sheets have everything on them that you are asking for. It is all on the cert sheets.

Emery The cert sheets that I am seeing don't go all the way down that list. I can trace it but you don't have that upfront when a material comes in.

Beckley The sheet as it is listed will, leaves out some items that are part of the system that aren't mentioned. There are items on here that won't be appropriate to something other than 5055. I think that you are focused on carbon phenolic, but prepreggers make many other materials, so if you are really proposing a sheet that has some universal usage, this sheet doesn't work.

Hill Some of the items would not be applicable, but if there are others that should be on it, we would like to know.

Beckley It hasn't been workable at the level that we work at, other than to provide what is needed by certification.

Hill Okay, but let me present this to you. Suppose, as we put this together, we wondered how we should use this and how we should implement this. Suppose a nozzle engineer specifies to his procurement people these items. They go out, and then it is specified from there, down the systems, and it goes to the prepregger. You see this and you know what the guy from Hercules or Thiokol really wants. Maybe you talk back and forth with him, but at any rate, there is an agreement as to what this material will be composed of with the constituents that are mentioned, and it goes all the way down the system and the material comes to Hercules.

Thomas I don't believe the buyer will know enough to tell you what carbon black to use.

Hill Suppose the engineer specifies USP 38?

Beckley Then he would get USP 38, but he wouldn't get 5055.

Humpherys Keith, could I suggest that the approach that Thiokol has used and the approach we expect to use on ASRM, will be to establish a document, a process control document, sometimes called a baseline document for each product and in that document, some of the information is proprietary and couldn't be listed on a sheet that would be sent in with a certification package, but that document controls all the ingredients, but also the process to make the product and that is an effective method of control, Don. Much of the information is proprietary and it resides at the vendor facility and is not part of the cert package, necessarily. Is that a valid approach? What do you think?

Beckley We are operating now on most of our programs.

Thomas But you know when you specify the resin SC 1008, you don't tell us how to make SC 1008. We give you SC 1008.

Beckley It reminds me a little bit of the fact that once a design of a motor is made, you don't repeat the motor design every time you start out to build another part. This page is just like, once 4926 is set for a given program, you are now saying, "make me another piece of paper and repeat after me what is there". I just see it as a degree of inefficiency that we are promoting.

Lutz That is not necessarily true, because 4926 can have CSA or CCA.

Beckley That is their prerogative and you accept that when you accept 4926. Our policy is that we don't change without changing the designation.

Thomas 4926 can use three different carbonizers as of past history. I don't think it does today, but if you don't want an Amoco carbonizer, you specify Hitco, and we will give you the Hitco carbonized cloth. If all three are qualified and you accept that then you can get any one of the three. All you have to put down on the purchase request is, "I will only accept X company carbonized cloth" and that is what you will get. If you want SC 1008 or 91 LD, you specify it.

Hill That is what we are saying. It starts out with the end users.

Drake In the case of fiber, you are probably using NARC rayon and it is fully qualified or nearly qualified to NASA, but it is probably not qualified on a number of Air Force programs, yet the product identification may be the same.

Beckley The charm of being able to buy 4926 is you will get the same cloth as a factor in the material rather than having somebody look at this list and they see 4926 at the top and they come down here internally and at Fiberite and this customer is saying I want a pick count of 17. Is that what 4926 is? Somebody is going to have to research and figure out, "Can we buy the cloth within that count?". We are building another layer of review in where I don't believe it is warranted subject.

Hill We heard yesterday that such things as heat treat affects the product.

Beckley For each of these cloths that are qualified, that product VCL, or CCA3, has had one heat treat level, as you are defining it, referencing that number. This study that ASRM has done has been to expand all our horizons to what is possible, fractioning it off to ± 200 , but once it is set, the intention is not to vary that particular parameter. It is only done at the research to pin down where you want to be.

Hill That is right. All we are trying to do with this is say, "Once this material is identified, it has these characteristics".

Thomas But the heat treat will vary according to your carbonizer, so if you want a Polycarbon cloth, it will be heat treated at that level. If you want an Amoco cloth, it will be heat treated at whatever they do. If you want a Hitco, it will be heat treated at that level. You have to decide which carbon cloth you want.

Hill We have time for one more comment.

DeVane You might try looking at this another way. If you are asking the carbonizers, the prepreggers to voluntarily begin a different data collection task than they have been doing, I can see that you will get some resistance. If you come in with a new contract and say, "In the future, here is how we want you to do things", there are going to cost impacts, probably, because it is a significant task, and you might get some response.

Hill Well, we are all under this continuous improvement, total quality management, quality improvement umbrella today.

Canfield I would suggest that the people review the documentation that exists today. I think it is out there, the documents are there, and I think, maybe, somebody

needs to look at the system today and see what is wrong with the system, because I think the information is out there.

Hill It is out there, but it is in disarray.

Canfield I don't think so.

Drake I think what we are really saying is that if you look at 5055 to a Thiokol spec, the Thiokol spec and the product designation would define each and every one of these, but it may be a different set of parameters than it would be if it was for a CSD spec.

Canfield Along with that we call out and control the product specs to the vendor. They have process specs. CCA3 is processed this way every time. If it varies from that, they write a discrepancy.

Upton This is a good discussion, but we do want to close this out as a task, so we do want to reach some agreement. We are not going to do that today. Basically, I want the interested people to get together off line and discuss this and see what is a reasonable solution. We need to take into account things like what Al said. Maybe it is a problem of just making sure that the right people are seeing the information. Maybe we need to adjust to take into account what you were

saying. We presented this as something that we had thought of and this is a task that was in process before I joined the committee. It does need to move forward in some fashion. We do need to form a subcommittee on this.

Humpherys Cindy, we did agree yesterday to convene a series of meetings at each of prepreg supplier facilities and that is going to happen in the very near future and the purpose of that will be to work this very issue.

Upton Could you take it over?

Humpherys Yea, if you are willing to use the ASRM system.

Horn Are you sure we are the appropriate people to represent this? ASRM is going to be different. We are single source down the line.

Humpherys I don't know if we are either. ASRM is going to develop a system that meets our needs.

Upton It will give us something to present to the group.

Beckley Who is the rest of the group? SPIP is the other arm of this. Some other customer has some other wishes and needs that wouldn't necessarily be on this

document. If we are doing this for RSRM and ASRM, he is certainly the appropriate representative. If we are trying to do it for something that is encompassing SPIP, I think the group should get a little bit bigger. If we are looking at all the customers over the time, the system that settles on a 4 digit designator that makes it easy to order material. It is different things to different customers.

Upton I don't think we ever intended just one universal generic sheet for absolutely everything in the world. That is a valid comment, but I sure exactly how to answer, because I am not sure what our scope of this task is. All I know is that we either need to take it off our books or do something with it.

Drake I suggest that Keith might be better suited to chair the committee activity on it. He seemed to be motivated.

Upton To work with Mark Humpherys? That is a good suggestion because you could bring in an outside of ASRM influence to whatever Mark's group is going to come to as a conclusion. Look it over from your point of view. Is that reasonable?

Hill That is reasonable. I'll pick who I want on the committee. How's that?

Upton That's fair. I do want to move on, but I did want to bring you up to speed about what we were thinking. I appreciate your comments. I want to know what you think. From the agenda, you can see that there are a lot of new things that we are trying to present today and we have a lot of really good topics to go over. I am going to rearrange things slightly. The HPLC test method is still very preliminary. It is something that I am working on at Marshall. It is being passed around. You see in front of you a very preliminary test plan. At MSFC we have an excellent chromatography lab that was empty, vacant and deserted. They had brand new equipment that was top of the line Waters chromatography equipment. It had all the bells and whistles. No one was around to work it. I couldn't free myself to go in there and really figure it out. I did want to set up and HPLC test plan to replace the GPC test plan in use in RSRM. HPLC affords a lot of opportunities that GPC does not give us and this test plan was developed by someone at a place called the Chromatography Institute. He did a lot of background work on all types of materials. He did a lot of literature searching and then he came to Marshall and spent a week and ran the materials on our particular equipment. We didn't get finished with the model compounds, but it is a start. What I want you to do is make sure that at least every company has a copy. I want to hear back from you if you have any comments on the test plan and, also, I want to know who out there has this kind of testing capability. Basically, just look at the test plan to see if you could copy that test plan if it

were in place right now. That is all that is for. I just wanted to send it out as a preliminary thing.

The next thing on our agenda is the NMR work. Dr. Tom Fisher is the first speaker on this subject. NMR has been discussed at the last two SPIP meetings. As you know it is a way to understand the fundamental aspects of the chemistry of our process. We are not proposing this as an online QC test, but we do hope that by learning about the NMR work, that we can improve what we would pick as an online QC test. After Dr. Fisher finishes speaking, Dr. Fisher is an organic chemistry professor at Mississippi State University, then Dr. Roman Loza of BP Chemicals in Ohio will begin speaking. He has also done some NMR work, but he will continue his talk with work that he has done in the areas of IR and DMTA. Some of you may know that the ASRM improved ablative ----- throughout the IR test for ASRM because it was fairly inefficient. Roman has done some innovative in dividing that task so that it makes sense to us. It is still a cheap, quick, easy test to do, but now maybe, hopefully, it works for us. Roman is going to update us on that. I am going to turn it over to Tom and Tom, when you are finished, will you just turn it over to Roman? Thank you.

Fisher It is a pleasure to be here. I started in January, so this is a new project to use NMR to principally understand some fundamental information about phenol formaldehyde resins and basically that is what we proposed to do. This talk will

involve three principal segments. We will start with model compounds, because I looked a little bit at the initial resin and saw how complicated it was and knew that I wasn't going to say too much fundamental about it until I knew what all the starting materials were. A lot of their spectra have been reported, but they were in a variety of solvents and I had to know exactly what was going on. We set up model compounds, like the methyl phenols, for instance. They are not specifically in PF resins, but you can purchase them all and I can get my data on them. I can then see what is going on, whereas the methylol phenols are involved directly. Then the second part moves on to the phenol-formaldehyde resin and in the contract I was asked to study three different resins, SC 1008, 91 LD and P39. I haven't seen P39 yet. I have seen three samples SC 1008 and one sample of 91 LD. We are going to start off with the prepolymer mix and look at various stages of the resin advancement., looking at the structure of the chemical compounds, the actual mixture of them, and changes that go on to see if we could understand similarities and differences, realizing that the cured resin, being solid, is not normally soluble. It has to be soluble to do liquid NMR.

This slide summarizes for you what happens when you first start making the phenol-formaldehyde resin. Phenol at the top reacts with formaldehyde and the phenol can only react at the two orthos and the para position, so we get the methylol phenols. You notice the numbers here, 1 through 6, are the principal methylol phenols that can be made in this process. We can put one methylol on

and get these two. We can put two methylols on and these are numbers around the ring. Then after we get these started, they can continue in the process chemically by splitting out water, for instance, between a para methylol phenol and another mole of phenol. That will give you the diphenyl methane because you have the two phenol groups and a CH_2 between them. This is a 4,4', a 2,4' and a 2,2' diphenylmethane. Then you will notice that this one was from both the ortho and the para, so there are multiple pathways to it. In addition to these three, of course, any of the other 6 on the earlier page can do the same sort of thing. So we get a very complex mixture of the diphenyl methanes as well as the methylols. As you go into the advancement cure, you get a lot more complications.

With that in mind, we wanted to purchase as many compounds as we could study by NMR. Carbon 13 NMR has been the principal method of choice. There are a few other methods as well, but Carbon 13 is still the major technique that we looked at. These are the nine compounds shown earlier that are directly involved. These are not model compounds, but are the specific molecules in PF resins. Commercially we could purchase the first three and the last three, but these three (4,5,6) were not commercially available. I found that TCI, a Japanese company, sells number 4. I ordered it at \$162 a gram and it turned out that when they sent it to me it was polymerized. The literature says that if you get any water in it, it will polymerize, so they got it back. I do have a student on the

project and he is trying to make these three, but I think you will see that our model compounds may make it less necessary that we have those three.

Of the rest of these 19 compounds in the initial series that I mentioned, the methyl phenols have the advantage of having all the positions needed. Instead of having the initial alcohol, the methylol on here, we just have the methyl, so I can model that one and see the benefit of these next six compounds. This methylolphenol is very close to the number 6 compound, only 2 of the three substituents are alcohols.

There are two segments that you see of these phenol formaldehyde compounds. You see the phenol part and you see the formaldehyde part. These are the phenolics that we have. Down here is the formaldehyde part and the part that you see here is the methylol part. I want to interpret these later so that you can see specifics. Then we go over and see here, these diphenylmethanes. You will notice very different ranges. These are low 60s, these are 30s and 40s, a completely different range. You could study them very easily, whereas the methyls themselves are in a different range, at 15 to 20 ppm. These are the three methylolphenols (4,5,6) that were not available commercially.

These are Carbon-13 chemical shift values. That is, each carbon in a molecule will occur at a certain place in the NMR, so we can look at that peak and say it

is a carbon. In phenol itself, there are 4 separate kinds of carbons. They are numbered 1, 2, 3, and 4, also called ortho, meta and para. These are the numbers you will see when phenol itself occurs. We can look at the NMR, look at these peaks and identify those explicitly.

I mentioned earlier about the side chains. Let's look at the side chains. Here is an ortho methyl group occurring at 16.1 ppm. Then if I look at where else I have ortho methyl groups, 16.1, 16.5, 16.5. You see that it is all in that same range. If I have an ortho methyl group, it is around 16 to 16.5. I know exactly where it is going to be and the para is similar. If I put a para on, it occurs at 20.4. In the similar compounds once we identify the ranges and where they are, then when we see a peak at this, we can say this carbon is involved at that position in the molecule and we have some identification of it.

In addition, some key peaks are the ortho carbons. That is, we have a carbon in the 2 position that has a hydrogen on it. We see that it is at 115 ppm, and we find such a peak, we can start saying something about the compound.

Utilizing that information and the three methylol compounds that were available commercially and as I say, all these numbers came from my solvent which was d_6 -acetone, which is the traditional one used here. An awful lot of literature reported they used D_2O . I wanted the numbers to be very accurate, and all at the

same concentrations. All were done under the same conditions, so I know my numbers are reproducible and I am not using a number from somebody who may have used different conditions.

Again, this is the same compound repeated, phenol, our starting material. We go down and we put this substituent on it. What we would say is, "What is the influence of the methylol?". Well, the ortho carbon now went from 116 ppm to 128 ppm. That CH_2OH group increased that number by twelve. There is an additivity parameter that chemists use and if you put a CH_2OH on a ring, the carbon that it is bonded to, increases by twelve parts per million. In a like manner, the one next door here, goes down by two, and so we can see that. Whereas, this one over here goes from 158 ppm to 157 ppm. The meta positions on there are not affected. These numbers are specific for our molecules. I can go look at the molecules that I haven't done and there is one particular region that gives us the most simple and the most important information on phenolics. That is the C1 region. This is the carbon with the OH on it, because in every phenol compound, there is only one of those and every phenol that goes into any resin or anything else, has one C1 available. It is in a distinct region by itself. So that gives us a lot of information.

Let's look at the formaldehyde part. It is easy to see that if you have a 30 ppm, it is here. If you have a 35 ppm peak, it is the 2,4', and if you have a 40 ppm,

it is the 4,4'. You can plainly look at that. Of course, this has been known, but I am reinforcing it here. The same thing that I told you about the orthos in the phenolic group hold. If you put together a two with a four, the two numbers are almost as reproducible in the 2,4', as they are the 4,4 compound. This completes the models compound assignment. We understand pretty much which compounds have what chemical shifts and how we can identify the individual compounds.

Let's go to the resins. In terms of the vocabulary I have been using, the methylol group is this group, a CH_2OH , an alcohol on there, the ortho, meta, and para positions. There are four distinct positions that the people normally look at in the phenolics. I emphasize this position here. Also, the meta carbons always have hydrogen on them because you never alkylate them. That is a wide range and it is a very cluttered range. There are lots of those around. Also in that range, you will see ortho and para carbons with a methylol group on them, or a diphenylmethane group on them. This range is a little bit broad. Then it is clear as to where the paras are as you saw earlier at 120 ppm and the orthos are at 116 ppm. So we have four phenolic ranges that we look at to identify.

We have likewise, four formaldehyde ranges that we look at to identify. The major components in these are formal groups, which is a methylene between two Os. This is a kind reservoir of where the formaldehyde stays before it reacts further. If you get a fresh sample, you see a lot of that. There is the methylol

region. There is the amine region, which is a CH_2 between an aromatic and a nitrogen. Then there is the diphenylmethane region.

I am first going to talk about qualitative assignments, about which compounds have what values, their actual assignments, and then I am going to try to quantitate some of this. For those of you who haven't seen a spectrum, this is what the carbon spectrum look like. This peak is at 20 ppm and this is at 160 ppm. The numbers I have been giving you are taken off a spectrum generated that looks like this, where the left half of the spectrum is the phenol half. The right half is the formaldehyde half. These are where the chemical shifts occur in the compound. The C_1 , the COH region, is between 150 and 160 ppm. There is quite a bit of information here. Then we have the meta region. We have the para region. We have the ortho region. We have the four phenolic regions mentioned region. We have the methylol region and the diphenylmethane region. In this sample, I didn't see much in the formal region.

Pinoli Tom, clarify a point. I thought I heard something that doesn't go with my thought process. Isn't the y axis the quantitative interpretation?

Fisher No. This is because of something called Nuclear Overhauser Effect. It is related but not on a one to one basis. The intensity of it is qualitatively how much you have.

Let's point out some major peaks because that is related. Isopropyl alcohol was added to this and these two peaks are the carbons in isopropyl alcohol. The other four major peaks are from phenol.

Pinoli We are talking about the y axis types aren't we?

Fisher I can quantitate the peaks on the y axis. To do this I have to use a forty to forty-five second delay and here I can get by on three to ten seconds. I can take this spectrum in about one-fifth the time as the other one and it tells me the same qualitative information, but it is not quantitative. It is related. This C_1 area is nearly quantitative, because there are no hydrogens on C_1 . Because there are no hydrogens, you don't have a NOE effect, so you can almost take the simple carbon spectrum and integrate that area (150-160 ppm). But your formaldehydes don't cooperate. They have two hydrogens on each of them and you have a big NOE effect and you can't quantitate that end. It is related, but not one to one.

L. Johnson From a qualitative standpoint it is very useful.

Fisher That is what we are doing here. It is qualitative. The peaks are all there, it is just not directly proportional.

L. Johnson The low intensity gives you a clue about the structure.

Fisher

Sure. If it is low, normally at that level, it means that the carbon doesn't have a hydrogen on it. Either that or there is not much in there. It is one of the two.

There are other methods of NMR. I am going to briefly talk about a couple of others, not with the idea that these are going to be better to use, but we wanted to explore other things. The proton takes you five minutes to run while the carbon is going to take an hour or two. There is not much information in the proton spectrum, but it is something that everybody can do and can do it fast. We don't need to overlook it, because over here you have the aromatic range. It is complicated. There are so many peaks that you are not going to be able to break it out. The methanol region is here and we see down here the diphenylmethane region. Isopropyl alcohol is in there and we can measure it quantitatively. In the ^1H spectrum, the numbers are quantitative. I can determine this number very easily because it represents six hydrogens and this is one hydrogen. So I can take out one-sixth of that and integrate it directly. I can get out of this the ratio of phenolics to formaldehyde. There is information here and there is other information we can get out of this. As the compounds get more complicated, it gets less useful. This is the simplest kind of NMR that we can do.

Pinoli

Tom, does your software allow you to go in and independently reduce certain areas and look for those relationships?

Fisher We can come in and expand any area, blow it up, integrate it. We have all the possible ways that you can data manipulate.

There is one kind of a spectrum, for instance, where, the assignments of protons have not been done. I told you what they were, but how do we know this? You can take a CSCM, chemical shift correlation map spectrum. This has the carbon axis horizontal and the proton axis vertical. I do a CSCM on all of the samples that I have done. For instance, these here are the three, the meta carbons of phenol. One here means that was compound one, phenol, and that is the meta carbon of it. This is the para of the phenol and the ortho 1 of it. All I have to do is look in this direction and find that peak over there and then I know that this carbon, this ortho carbon, and this ortho hydrogen are bonded to each other. It is that simple to interpret. You don't have to know anything about NMR to interpret them. When I have all these numbers, I can go back and see where they are. If we know the carbons, we can come back to the hydrogens and there is some hydrogen information because when I tried to figure the compound components of the resin, I did the hydrogen. I always do the hydrogen. This is a two dimensional type NMR and it takes a longer time.

This one is what is called a double quantum filtered COSY, and it is of SC 1008. You may not be able to see that too clearly. You see there is red and black involved and that means it is a phase sensitive method. A phase sensitive method

takes longer but shows you more information. What we have across here is a hydrogen spectrum of the aromatics, i.e., the phenols were very close together. These are the phenols in SC 1008. They are across here and the same thing up here is just repeated. The way you interpret this uses the diagonal line. This diagonal line through here is identical to the one dimensional spectra. It doesn't show us any additional information. Then the cross peaks. If I take this one and this one, this peak here is off the diagonal, so we call it a cross peak. Then I go down here and over to here to see where it is and that tells me information about where it came from. Well, what sort of information are we talking about? This information comes from coupling constants. The coupling constants on the phenolics and that is all it comes from the phenolics. I can't do this on the formaldehyde side. If I have two ortho hydrogens on the phenol side of the aromatic range that are adjacent to each other, they split each other into a doublet and this utilizes the coupling parameter to generate the spectrum. Now a meta coupling is a smaller one and the para one we don't see. We never see para hydrogens since they are not coupled. I can look at this and tell that this is the ortho methylol phenol. This is qualitative information, but in this way I hope to use it is as we get to the advancement of the resin, where we have higher molecular weight compounds. This is still a very sensitive method. It doesn't take much to sample. I can identify segments of the spectrum that have 2,4 patterns, 2,6 patterns or any patterns they have. I also did this on all the model compounds. I can overlay them and I can identify these. The five compounds

that I have specifically, I can identify here. Phenol is right in here. The para methylol phenol is in here. What good this is going to do me is yet to be seen, but here is the 2QCOSY of SC 1008 and one of is 91 LD.

This experiment shows you that I made a mixture of all five of the compounds I had that are actually in the mixture of the resin, phenol, the ortho and the para, and the two diphenyl methanes. I didn't put the ortho, ortho in because it is not found in the mixture. Instead of doing them all individually, I have got them all here at the same time. I can tell where they are and the pattern that they come in. I think this will be useful in my later studies.

This is the 150 to 160 ppm region, which is the region that represents C_1 . This is the carbon that has the OH of the phenol on it. This is the region that I mentioned to you that gives us total phenolics. Because I have these five reference compounds, I physically added them individually to this sample. This is called spiking in GC or LC. Look what I saw. Compound two increased. This is the resin itself and you look at the relative types of all the peaks here. This one is small compared to phenol. This is phenol over here. I can tell that is compound 2. There is no question about it. It is the compound that I added to it. I did that with all my references. The para methylol compound 3 was added and it is here. Likewise I added the 4,4'. That has two carbons so when you quantitate it, you have to take half of the mole ratio. These are mole percent

ratios that you get out of NMR. I can identify exactly which compounds that I have and not just guess on them.

In this sample called 6 Mix, I put in isopropyl alcohol in a mixture of all the components I had earlier. It was like the one I showed you, the red and white one a while ago, except it has one more component in it. I put in isopropyl alcohol. I found out that, in effect, it has some solvent influences on the peaks. I needed it there so the numbers would look closer.

What I am doing here is I am going to go through those areas of the phenol carbons and the formaldehyde carbons and I am going to show you that now of the five components we have, we can identify specific peaks of each. For instance, those five compounds are now identifiable very easily. I showed you earlier, but this is phenol. This is ortho methylol phenol, compound 2. This is compound 3 that we have from the assignments up here. This is compound of 7 and 8. From my numbers, these are probably compounds 4, 5 and 6. I am pretty sure of that. I know they are in there and from my theoretical calculations, I told you that this should be the 2,4 dimethylol phenol, the 2,6 dimethylol, and the 2,4,6. Those are exclusively assigned. These were the methyls that you have. This over here is a carbon with a para alkyl group on it and all the rest are metas. This is the ortho range. That is the para range. In a like fashion, I can

identify more than three-fourths of the peaks by reading the compounds that I have shown you.

Going to the formaldehyde end, we remember that the ortho methylol came at 62 ppm and the para methylols at 65 ppm, we look at these peaks and see the ortho peaks and the isopropyl alcohol. Likewise we go down into the diphenylmethane/formaldehyde range. Remember the 2,4' methylene came in this region in compound 8. You can find up here compound 7, the 4,4' compound.

Pinoli Tom, can you go back to that? The choppiness on the line suggests that you are measuring at the limit of the equipment, isn't it? That accounts for the choppiness. Your concentration level is so low.

Fisher Probably not. That is probably conformational differences of different compounds. When I make these initial resins, I put in as much as I can. I get about a 40 percent solution of them and even though the components may have one or two percent in it, when I run it, I can see it them.

Thomas Tom, do you make up mixtures of the resins yourself?

Fisher Well, I had my commercial compounds. In this six mix sample, I took the six compounds that I had and I put 40 mg of each of them in it and then I put in a little more of isopropyl alcohol. I didn't try to match the mixture because I didn't know how much was there. I put an equal amount in so I could come back and quantitate, because then I knew the whole amount of each and I could look back at them

Boudreau Your six mix is an equal weight mixture?

Fisher Yes.

Pinoli You can't calculate the mole ratios?

Fisher You can calculate them.

Thomas Would there be anything to gain by using production resin?

Fisher These are production.

Thomas I thought you said you were mixing them.

Fisher This is my six mix sample. Below it is the production resin.

I mentioned to you that the 2,2' diphenylmethane is not in there. The d₆-acetone comes in the same place. You can't see it. Here I took the SC 1008 and you can see the 2,4' and the 4,4' is there, but it is not here. It is plainly not in that resin.

So far it is qualitative, but we have identified a lot of things. We know what we are looking at. This is trimethylphenol, our standard. The beauty of it is that you see one peak here and it appears at 151 ppm.. It is out of the range of everything else. Nothing else is on the right side. Phenol is on the left side and everything is in the middle. The other hydrogens on it, include two methyls, but when you quantitative carbon-13 spectrum there are two of these and there are also two methyls in isopropyl alcohol. I can look at that directly and say how much isopropyl alcohol it had. This makes it particularly convenient. I can quantitate my phenol from here, formaldehydes here, and isopropyl alcohol here.

Here I put in fifty mg of my standard. I know exactly how much it is and this is spectrum SC 1008. This is an integrated sample. The intensity values of 101 and 151 are directly related, which tells me phenol on a mole basis, had 50 percent more than my standard. I can now quantitate that number. I can take all eight of the assigned peaks that I have and I can quantitate them and tell you exactly how much of those major eight components that we have in both the SC 1008 and 91 LD resins. This shows you the advantage of that standard. These are the two methyls of the standard. These numbers should be about two to one

there and that shows whether or not the experiment is integrating right. Then your IPA is over there. It is ninety-nine and one-half. I know I had fifty mg of this and this related to that number on a mole ratio directly. I get my numbers on a mole ratio. These are the quantitative numbers here from the two actual samples that were sent to me of SC 1008 and 91 LD. These are given as on the table as weight percents. I did all the calculations for you. On compounds where you have the 4,4', you have two of each carbon in there. I have done all the chemical calculations and taken that out, but these are the findings that I have from the two samples that were received. Of those eight components, this is the phenol, itself, the ortho methylol, para methylol, 2,4, 2,6, 2,4,6. This is the 4,4', diphenylmethane and the 2,4'. Isopropyl alcohol is down here and would be about 22.5%. Over here it is about 13.6 percent in that sample. The free phenol was found here to be 12.9% in this sample and 15% in that sample. You can likewise go through the independent compounds that we have in there and look at the relative amount of the individual compounds.

Okay, now what I am doing is looking at the C₁ region. This is SC 1008 and this is 91 LD. We are looking at which compounds are the same and which compounds are different. We quantitatively look at those eight, now there are some others outside those eight. What are they? I match them up. The SC 1008 has a few less peaks in it. There are some differences here that we can see in the phenolics. If we look at the meta carbons, you can also see differences. This

is the ortho and the para range. This reconfirms what I said before about the additional orth ocarbons with hydrogens on them. I think there are para alkylated compounds in there.

I haven't shown you any of the formals, but they tend to be there. There are three of these that tend to come in. This is basically a reservoir of formaldehyde and I think it is one formaldehyde added to a methylol group to form this group. That is a reservoir of formaldehyde that they use up very quickly.

The major difference that I see is the amine region. The amine region in the SC 1008 is almost blank. You can't see it. When you go across these integrated areas, I have blown these up way big. The position of the aromatic amine comes in much more down here. Of my total integrated formaldehyde region, I get around 30% of this 91 LD and I get about 12% up here in SC 1008. I suspect that some of those compounds that I could not identify at that para position up there are really parahydroxybenzylamine sites. That is my first guess. I am just basing that on the intuition of what I know so far.

L. Johnson Were you able to pick up any free formaldehyde in the SC 1008 or the 91 LD as received?

Fisher I consider free formaldehyde to be the formal group. I see more in 91 LD than in SC 1008. I am not sure the SC 1008 sample was fresh and the 91 LD came to me on dry ice and I knew that it was fresh.

L. Johnson Roughly, how much was in there?

Fisher 1 to 3 %, roughly.

Bhe Could you pick up the residual phenol?

Fisher Yes, the residual phenol was 13%. The phenol can be quantitated very easily. You can look at just the carbon-13 and that 158 peak is phenol, free phenol that is unreacted. That is the easiest thing to do.

Bhe What about the content of the free phenol?

Fisher It was 13 to 15%. How much different are batches? That would be interesting. If somebody has a sample of P39, I would appreciate it.

Loza Last time I gave a short overview of what we were doing in the area of phenolic resins. This time I will try to give you a clearer picture of what we are doing in terms of characterization of the phenolic resin. Here is an outline of my talk

today and I will talk a little bit about phenolic chemistry. We have done some NMR work and some FTIR work. I will talk a little bit about aging studies in 91 LD and that may answer some of the questions that were posed on what happens to the formals and the unreacted phenols. Then I will talk just a little bit about correlating IR with NMR data. Then we will move on to talking about prepreg analysis and show how the material changes. We will talk a little bit about some experimental prepreg where the prepregging conditions were changed and what happens to the resin under those conditions and then wind up with some general conclusions. Some acknowledgements, the work on the NMR was done by Bob Boyer. Mary Ann Hazel did the IR work.

The reason why we became involved in this area is summarized here. We wanted to develop NMR and infrared techniques that would be able to quantify the degree of advancement in phenolic resin. At the same time we wanted to compile a data base on the different materials that F&M was receiving, both SC 1008 and 91 LD, to find out how much variability there is in the resin for batch to batch and lot to lot. At the same time, we wanted to understand the chemistry of the phenolic resin to help people design prepregging conditions, etc., a little bit better.

Here is a general schematic view of how I envision the phenol formaldehyde condensation reaction occurs. I start out the phenol formaldehyde and some type

of catalyst, in this case an amine catalyst. Initial condensations have been described, followed by methylene bridge formation and on to cure to form a crosslinked system where you have not only methylene bridges, but also ether bridges and a host of 3D structures.

Here is our spectrum of one of the phenolic resins. We have gone through it and assigned all these peaks. This is to remind us of what regions we are interested in. We are interested in the aromatic CO carbons. We are looking at para unsubstituted ortho unsubstituted, the formals, the methylols, the amine derivative, the methylene bridge materials and the isopropanol. What we tried to do is to, without going into a lot of detail, this particular component was present there from an analysis of lot to lot variation, and we needed some sort of quantitative measure of what materials are present in each lot of material. What we do is measure a series of ratios; rather than using an internal standard, which takes longer to do because we have many, many samples to analyze. We tried to analyze, at least in triplicate, each lot of material. To date, we have analyzed over twenty lots of 91 LD and probably 7 or 8 lots of SC 1008. What we had was a ratio of the different types of formaldehyde and what we could come up with is the mole percent of various species. We could come up with a formaldehyde to phenolic mole ratio to see how well the composition is controlled the composition is from lot to lot; how much solvent is present; how much unreacted phenol is present relative to the total amount of phenol; and the degree

of unsubstitution of the phenolic rings. These unsubstituted positions can further react. We have found out that you can look at the resin from different lots and see changes. I can look and monitor reactions in storage. The two different resins (SC-1008 and 91-LD) have two different chemistries. We can compare them.

In addition to NMR, we are looking at infrared as a more convenient tool for detecting changes in structure. In particular we are looking at two ratios in the infrared, without any solvent evaporation. The way we run out IR is to take the sample as received, run the infrared and then do a quantitative analysis and measure of two ratios, the 1024 to 1000 and 826 to 1000. Tentatively we have assigned this as a ether and probably a formal to aromatic methylol ratio and a phenol plus a para substituted aromatic to methylol ratio. Because we have many different components present, the assignments are a little bit ambiguous. There is some overlap that is possible. We have found out that resin advancement can be monitored very nicely with the infrared as well as lot to lot variation. We may not understand exactly what the differences mean, but they are real differences.

Here is a non-quantitative comparison of 91 LD and SC 1008. The isopropanol ratio is different, meaning the amount of solvent is different in the two resins. This is fairly obvious from the difference in the viscosity and the solids level.

The formaldehyde to phenolic mole ratio is similar. Degree of ortho and para substitution: ortho is similar and para is different. Infrared spectra of the two materials is different, reflecting the difference in composition. The formaldehyde is distributed in a different fashion. Methylol levels are different. Methylene bridges and amine bridging levels are different, but the free formaldehyde is similar. That is a quick overview of what those two materials look like.

Let's move on to our aging studies. In this set of experiments there was some concern about what happens on storage of the material before it gets prepregged. What kind of compositional changes take place? So what we did is we aged the material at room temperature from one to ninety days and monitored the infrared ratios. We also monitored degree of advancement by NMR, particularly looking at how the formaldehyde distribution changes, the different compositional species that are present, as well as how the phenols substitution pattern changes. NMR is more difficult to do on a routine basis. IR is a little easier. The measurement that is easiest to do is viscosity. We measured all three to see if there are any correlations between or among the three.

To make a long story short, here are the general trends that we see. The formal content, which is the reservoir of formaldehyde, drops to zero after a finite period of time. This depends on what the starting concentration. Usually after about 15 or so days at room temperature, that level is down to a level where we can't

measure it. Since this is dropping, something has to be forming. These two things formed, the methylol level increases and it increases slowly. There is a linear increase in the methylene bridge species. They tend to increase at linear rates from zero up to ninety days. That is a nice way of following the degree of advancement. Percent of unsubstituted phenol first decreases, because what free formaldehyde reacts with phenol then levels off. The amine bridge species does not change. That is understandable since we are not adding any catalyst to the system. Degree of ortho substitution, again, increases and then no change. That comes from the fact that you are making ortho methylol. Para substitution, there are two rates. First it is fast and then it is slower. Again, I think this reflects methylol formation followed by methylene bridge formation. The formaldehydes to phenol mole ratios should not change. That stays the same and then there is no change in the solvent level because it is a closed system. There is really no surprise at what is going on here. You are finishing off what you didn't finish in the reactor. Those were the NMR results.

Here are the infrared results. This is something that is a little easier to do from a QC point of view. We see that the 1024 to 1000 peak ratio decreases with time then levels off. The 826 and 1000 peak again increases with time and then levels off. I want to show you the overhead of those two traces. The 1024 drops and then it is steady. They are fairly good fit of lines. The first one has a r^2 of 0.94,

and for the 826/1000 ratio, the fit isn't as good. There is a lot more scatter, but the general trend is upward. Here is a fairly easy way of following resin aging.

The easiest method of all to follow resin aging is looking at viscosity. What we have done here is something a little bit different. We are measuring the viscosity but then we are dividing by the original viscosity. What we really have is a relative viscosity with time. That increases linearly from 1 to 98, so it is a nice straight line. Here is the slide of that information. There is an r^2 of 0.99, almost. This is on five separate lots of resin, so this is not one resin which would give you a much straighter line than five separate lots of resin that have been aged ninety days. It is not only within lot, it is lot to lot, that gives you the same general trend.

What happens on room temperature aging? As I said before, what you are doing is finishing what you didn't do in the original reaction, using up the unreacted formaldehyde which is stored as formals. Now we understand a little bit more about the chemistry on storage and advancement. What we wanted to do is find out, and we saw some correlations between the NMR and FTIR data. What we are going back and doing right now is to look at all the data from all the materials that we have. We have almost twenty sets of lots of 91 LD and we are going back and looking for linear correlation of the data. Right now we have identified two and that is a 1024 to 1000. We feel strongly that has something to do with

disappearance of ether functionality, in this case the formals. We are looking at changes in formal content of the resin and the correlation here, the r^2 0.93. 826 is a little less certain, so that may be complicated by some other factor. Again the 1024 on as received material has a 0.78 correlation for 91 LD and a 0.92 correlation for SC 1008. I think that it is fairly obvious that what we are doing is picking up in the 1024 to 1000 peak ratio, the unreacted formaldehyde and its variability from lot to lot. On SC 1008, there seems to be a little bit less variability from lot to lot on the 826. This could be in part due to the smaller sample sizes. This here could be relative to a larger sample size. We are continuing to find different types of correlation and we will keep you updated.

Now we wanted to look at some commercial prepregs since we understood the aging phenomenon, at least at room temperature. What kind of aging do we see on prepregging?

Croese Does humidity enter into this in any way?

Loza In what sense?

Croese Did you control humidity in your testing?

Loza It is in a closed container in the aging experiments.

Croese Okay. You don't know what would happen....

Loza You wouldn't be leaving the resin out in an open container. This is what happens when you move the material out of storage, cold storage and put it in production facility, and before it has been mixed. We wanted to find out what kind of aging...

Croese So you always keep the lid on the can?

Loza Oh yes. It is a fire hazard if you don't.

How far along in an advancement process are we compared to prepregging is the question I wanted to answer by this experiment. We took some commercial prepreg and we extracted out the resin and we ran the same test that we would on the as received resin and what we see is that the methylol content is much lower in prepreg material than it is in as received resins. Maybe there is a hint of some ether bridges. There are some small peaks that have been defined in literature as ether bridges. We don't have any confirmation on those. We see a big increase in the methylene bridge content and especially what we see is the ortho para splits into two types of methylene bridges. Here ortho para bridges are dominating. The unreacted phenol content decreases significantly. That is

either due to reaction or to volatilization of the phenol during prepregging. In volatilization the formaldehyde to phenol mole ratio goes up. The only way we can increase it is to add more formaldehyde which doesn't have it or reducing the amount of phenol. I think that is why I feel there is some phenol being lost in the prepregging. Finally the ratio of 826 to 100 increases.

For example, here is an analysis of a composite 91 LD, unaged, aged and then what it would look like as a prepreg. The mole ratio here, probably nominal from starting, is still nominal over here. The prepreg has gone up by twenty percent. The formal content is of nominal value here and it is zero after aging and zero after prepreg.

Thomas What is the time between the aged and the prepreg?

Loza This is two different things. We are not prepregging aged material. This is just a comparison of what happens on aging and what happens on prepreg. This is no one particular 91 LD. This is an average value I used out of 18 or 17 lots of material.

L. Johnson What sort of variation do you get there, from lot to lot?

Loza That depends on what you are interested in. This standard deviation here is ten percent of the nominal value, or maybe more like thirty percent of the nominal value. This may vary by fifteen or twenty percent, something like that. It is on the order of ten to fifteen percent on an particular measurement. There is an error associated with just the measurement.

Bhe What solvent do you use to dissolve the prepreg?

Loza Acetone.

Bhe When you dissolve that prepreg, does all the resin completely dissolved or does some of it stay on the prepreg?

Loza I can't tell you on these, in this particular case. I think we are getting what is the nominal content.

Singer Do we understand correctly that the change to the prepreg is astonishing?

Loza There is a big change, yes.

L. Johnson I don't know that I would describe it as astonishing.

Loza Compared to room temperature aging, yes.

Beckley It is significant in some of those factors, relative to the aging phenomenon.
There is a lot of change.

Boudreau When you consider you are comparing room temperature aging against a higher temperature exposure, I would suggest that, perhaps, take the prepregging element out of it, if you were to age resin on the elevated temperature, you might get the same picture that you have on the prepreg, perhaps with the exception of the mole ratio change.

Loza Yes.

Singer Is that experiment going to be done?

Beckley Bob, what I was describing is if you take that 826 to 1000 ratio, the total change in aging might be from 0.9 to 1, but if you take the change from prepregging it from 0.9 to 1.3. As far as that number goes there is a larger amount of movement than we would expect to see in any aging phenomenon.

Thomas Wouldn't you get a similar movement from aged to prepreg, Don?

Beckley I think the answer to that is yes. All you do in the prepregging process is compensate for whatever issue you didn't have happen along the way before you started. The end point is the same. You are headed to an end point, so you merely adjust the process to bring the product that you want into that conformance.

Ma Have you tried aging the prepreg to observe the changes?

Loza We haven't done that. You will see in a minute that in the experimental prepreg that they were staged for different periods of time and there are differences that show up there. There are major changes that happen here. I think the point was does room temperature aging approach anything like you would see in prepreg and the answer is no. I think the point here was are we going to, by exposing this to room temperature for two or three weeks, overcompensate or overshoot what the prepreg is. The answer to that is clearly no. The prepregging is much more severe in terms of advancing the resin than exposure to room temperature.

Bhe If you have some of your resin that doesn't dissolve in the acetone, would you expect the same results?

Loza I'll show you in a minute what happens when you don't.

Singer Did this prepreg have a prewash?

Beckley Probably.

Loza There was some concern about the workability of the prepreg and try to get a handle of what workability and the elastic properties of the prepreg. What we did was some DMTA analysis. It is the same technique that was described yesterday. This measured the properties as a function of temperature and in particular the storage and the loss modulus as well as the tan delta ratio. What we are looking for are different transition temperatures, especially the E'' maximum temperature and the tan delta maximum. This is related to the glass transition temperature of the resin. What we wanted to find out was what is the glass transition for maximum pliability and then use this information to monitor cure. I'll just show you one example of a commercial 5055 material.

You can see the two transitions, double prime occurs at 41° and tan delta maximum occurs at 94° and down here is where there is a change in properties. That gave us an idea of where the material would be most fluid.

Singer What was the heating rate?

Loza I don't remember, about four degrees a minute, something like that.

We are interested in how the position of this peak compare with the temperature change upon varying the staging.

L. Johnson E" gets pushed to much higher temperature.

Loza F&M made some experimental prepreg where they took 5055 phenolic mix and put it on the glass fabric. Glass was chosen because of the low variability of the fabric. We wanted to look at the resin not variability of fabric. It was prepregged under very mild conditions. They were stripping a small amount of the solvent off without advancing the resin. Because of the difference in fabric, the resin content is lower than some of the numbers you would normally see. The prepreg was then cut into smaller pieces and heated in an air circulating oven. The variables were time, temperature, resin age, and prepreg age.

Normal responses were measured, including the workability of the material. Then on selected specimens we looked at the NMR and FTIR and DMTA to see how time and temperature exposure changed them. We tried to correlate some of the visco-elastic changes with infrared and NMR changes.

Here are four samples that we have looked at so far. I have noted temperature A and B. A is lower than B. Here is resin solubility. Here it is 100%. For these three it is essentially 100%. We know we are getting the resin off. Here

it is 62, so some of it is being left on. That addresses the earlier question. Low numbers, they are not typical of what you would see, because this is glass fabric. I think what you were saying before is that temperature and time and temperature increase will see the E'' maximum moving to a higher temperature. Obviously you are starting to advance it further. The tan delta maximum, you will see a single peak here. Here are two transitions from these two samples and that is moved way up. You have partially cured the material here. Infrared ratio, again I think there is an interesting story here in that one ratio may be a little more indicative of what is going on than the other ratio. There is little change here. The 828 to 1000 is well within experimental error. There is a change here. You see that there is a difference in the percent flow of these two materials. This ratio is telling us that something is going on.

You can look at NMR data and what I have done here is try to compress all that NMR information into one index or two indices, the methylol index, which is the ratio of the number of methylol groups to the total reacted phenolic present as well as the methylene bridge index which is the number of methylene groups to the total of phenolic carbons. We see that ratio is dropping here. These two are fairly similar and that may explain in part what is going on over here, but this ratio, the methylene bridge is higher here and lower here. This may be telling us something about the system that is not evident. There is a structural change that is responsible for the difference in the visco-elastic properties of the material.

If you cook it too long, obviously, these ratios will drop dramatically, and this one shoots up, and now you have partially cured the material. The question is now, "Where does commercial material fall?". It probably falls in this range here.

Beckley Roman, the only issue I see there is the commercial tape grade material, the 826-1000 index is for tape grade is nominally about 1.15.

Loza You measure yours a different way.

Beckley Well, okay. If you say that is somewhere past...

Loza Yes, it should be somewhere in here. The point that I am trying to make is that these transition temperatures, DMTA, which is a measure of the visco-elastic properties of the material. I think they are directly relatable to the molecular species that are present.

Beckley Maybe another way of reflecting it is the soluble resin portion up there of the commercial tape grade material is still about 100%, 99%.

Loza Yea.

Beckley So your 62 material, accordingly, should be well past...

Loza Yes, this is well over cooked.

Beckley Okay.

Bhe Do you still have insoluble resin?

Loza I can't even begin to answer that question because there is no way of looking at it.

Boudreau Qualitatively, Roman.

Loza It could be the same as this material. It could be very close to it. This is the soluble portion and so the insoluble portion is probably very similar to it. The problem is, in commercial material, you are dissolving all of it, or essentially all of it.

Bhe That depends.

Beckley In that 826 to 1000 ratio, it may have even been higher. The stuff that was left was the 1.05.

Loza This is the stuff as it is still extracting. Unextractable material is probably 1.05 or higher. Probably higher. Again, it is like trying to find out what you can't. Is this really relevant? Material that is partially cured is not what you get on a commercial prepreg. You are extracting out essentially all the resin that you are putting on.

Bhe What do your double and tan delta temperatures mean?

Loza There are two transitions. We don't know exactly what they are. We could have two types of polymer that are present, one that is a low TG material and one that is a high TG material.

Bhe You are doing the blending, then. Are you blending the two resins?

Loza No. This is the resin itself. It shows two peaks and what you may have is a lower molecular weight material that has a tan delta of 40 and a higher molecular weight material that has a higher tan delta, a glass transition temperature that is higher. It is two peaks. We don't know exactly why. We may be able to separate those two materials out and look at individual components, but for now all we know is that there are two peaks. What we are looking at is resin advancement, vis a vis staging is what we are looking at.

- Bhe I understand that but, generally, if you stage it you start with one resin and you stage, you get one peak, not two peaks. Bob, can you comment on that?
- Boudreau I have nothing to add to that other than the obvious that when it is relatively green, there is a single peak. As the material gets more complex, upon curing, it's better that there are two peaks.
- Beckley Didn't that happen because, effectively, the viscosity was dropping at a predictable rate and then the slope changed. Effectively, the temperature was increasing, so the tan delta is a derivative of that shows, what in effect is, a second peak due to a viscosity change.
- Loza The tan delta is really the ratio of the E'' to E' . It is attributed sometimes to glass transition, but it could be a component of the material. Some of these peaks are transient. They show up in one sample and not another. I wouldn't read too much into that. I think the bottom line is, the material becomes less fluid as you advance it more and that is reflected in the percent flow numbers. That was the whole issue here, how can you make material less or more stiff. Time and temperature were the answer from these simple minded experiments.
- Singer Would it be an outrageous exception of the logic to say that kind of result is what you would expect if you had a mixture and more than one compound is present?

Loza Oh, yea. You do have more than one compound. You have a multitude of compounds present. You saw how many different components are potentially there, just from the model compounds. Now add to that the presence of a catalyst which has its own structure associated with it, so you have on the order of 20+ species that are present which are all starting to interlink. You have a very complex heterogeneous polymer. This is not like looking at polyethylene as a homogeneous homopolymer.

L.Johnson Those As and Bs you have up there, are they proprietary?

Beckley For ease of coding of ranges.

L. Johnson What sort of generic ranges of we talking about for As and Bs?

Loza Forty degrees and up and I forget the time exactly.

Beckley The starting prepreg was a very early B staged material.

Drake Many of the contractors that we deal with have specifications that says the prepreg manufacturer shall certify this material to be good for six months and our guy says good for a year. In many cases we use the material for two years or three years. Is there any way of standardizing that, or extending the initial vendor certification for shelf life?

Beckley I think you are posing a question that seems like this advanced technology can answer with the proper set of experiments and that, namely, is what is the change in these species with time. You are really getting into a question that is financial. Who wants the obligation for that material over a period of two years? There is one aspect in how long is it good for. I think I have told you before that 15 years later I have laminated this material. Its shelf life is really quite long left at room temperature. How long is it good for?

Drake Shelf life becomes a financial obligation issue.

Beckley That's right. It effectively, it is not a simple question.

Drake We had material that would sit out in the sun for two or three years and make outstanding brakes.

Beckley I understand you were dealing with a designer for an advanced prepreg, an advanced B stage material as your starting point for that. A man who fabricates vacuum bag laminates that has a very light B stage, a very early material with that 6 or 8% vol, he takes the polyethylene off and six hours later, it is no longer usable for his application. The question again on the spec for a given material, is how long is it good in that application?

L. Johnson Was differential scanning calorimetry considered?

Loza We didn't do it.

Upton It has been done by other testing organizations.

Loza To summarize on the experiments for resins, the standard tests will decrease as the resin advances, the flow decreases, the tan delta maximum goes to higher temperatures, prime goes to a higher temperature. The methylol index decreases and the methylene bridge index increases and your two IR ratios increase. There is some good correlation between the NMR and IR data.

Here are some of our conclusions. I think that NMR is a valuable tool for studying phenolic resins. It provides detailed information on the structure. If done right, it will give you quantitative information on resin advancement. It gives you an idea of how resin composition changes from lot to lot and within lots. FTIR is a convenient tool and then when you couple these two together, you can find out what is happening here and the FTIR reflects those changes. It is easy to use and it can be used to follow resin aging in staging as it has not been used in the past. Viscosity is a very convenient method for measuring resin advancement. You have to know what the starting viscosity was. Lot to lot, it is less useful due to solvent changes and compositional changes. But once

composition is fixed at the reactor, viscosity is a very convenient way of measuring advancement. It is linear from 1 to 90 days of aging. DMTA is a good way of determining the visco-elastic properties of the resin. Resin advancement follows a finite reaction pathway based on the phenol formaldehyde chemistry that we reviewed earlier. That's all I have. Thank you.

Upton Thank you, Roman. We are pretty much right on schedule. The next thing that we have is a presentation by Ken Drake of the Aerospace Corporation. Ken has been doing some work on an inhouse data base that we could all access at each meeting, simply by exchanging MacIntosh disks on an Excel program. Ken started this work last fall and he is going to give us an update.

Drake I would like to acknowledge that this program is sponsored by the Aerospace Corporation in the form of Engineering Methods and also the Air Force Space Systems Chief Engineer's Office. The principal investigator on this program is Dr. Wayne Goodman who works for Dr. S.R. Lin. They have both been very helpful. I would like to thank the SPIP committee and all of the suppliers who have been very helpful in providing data to load this database.

One of the problems we face is the designers and analysts understanding exactly what is FM 5055 or 4926. What is the pedigree of it? In the way of background, a few short years ago, the design of nozzles was a black art. A few

people like Don Hatch went out in the shop and made a nozzle and it worked much like the Surveyor nozzle that Vic talked about yesterday. But we find now that the data base and the amount of testing is grown substantially. If your office is like mine, you probably have a file cabinet or two full of data, and you can no longer find what you are really looking for. Testing of the nozzle insulative and ablative materials has become thorough. The amount of the available data that we talk about has grown drastically. It is at the point that you can't really keep up with it. The product identification code makes it difficult for the designers and analysts to understand the data. MX4926 or FM5055 can be one of two rayon suppliers, and maybe next year, that could even go to three, not knocking NARC, It is just the history. You have Highland or Milliken. You have three different carbonizers and in some cases you can have low, intermediate, or high fired rayon. As we learned yesterday, you can also have low-intermediate and high-intermediate. The engineers need to understand this for their analysts.

The ablative data base material that I am talking about is a carbon phenolic constituent material acceptance test and tag end testing. This is a Microsoft EXCEL program which can be used either on the MacIntosh or the IBM-type PC. We are cataloguing constituent material pedigree, test methods, environment and temperature test, tag end tests, receiving tests, as well design allowable data. The design allowable data has been generated by SORI and other people. The EXCEL program will communicate with the M/Vision program and I think that

after I get through, Greg Crose and Curt Loomis will give you a demonstration on the M/Vision program. We would use this database to load the various finite elements models and codes. We should be able to do it quite uniformly, where as now the guy has to make a series of assumptions of what properties to use, etc. We hope to automate this and save time and labor and schedule time.

Singer This is a result of that and you can make your assumptions without any thought at all.

Drake No. Quite the opposite. The purpose of it is so we can make the assumptions once, very correctly, not without any thought. In other words, you can consider the problem, make the assumption and always have the same assumption.

Lutz Why did you choose EXCEL which stores all the information in one large file as opposed to a database, such as dBASE, RBASE, something like that.

Drake It is the way we started the program and I can give credit to the Air Force who made a thermal plastic database where I got the idea from.

Upton A lot of us use EXCEL already.

Drake A lot of us do have EXCEL already. It is a very common program that you can use.

Lutz EXCEL is very limited as far as a large database. It is column limited where as dBASE has many, many fields and is a couple million records limited as opposed to a program like EXCEL.

Mill You are going to rapidly come to a limitation on EXCEL or QUATTRO PRO or LOTUS.

Drake We are using EXCEL to feed into M/Vision. M/Vision is the larger database you are talking about.

Lutz Is M/Vision also compatible with dBASE?

Drake I don't know that.

Upton They are saying yes.

Drake The core of the EXCEL program would be these areas. We have instructions telling how to use the particular guidelines and glossary of terms. Data items on it will be referenced to a file that you can get and cross check yourself, a list of

the participants. I have in the menu a product flow, hopefully starting from raw rayon and a basic understanding of how it is made and going through all of the various elements to the finished composite in some form of a standard flow time. The rayon yarn, the cloth, the carbon graphite, the resin, fillers, prepreg and finally the tag end test is part of the data base as we now see it. At this point I have a very substantial amount of data that needs to be catalogued and we are working on it. That concludes my program.

Upton Thank you, Ken. Next on our agenda is a presentation by PDA Engineering on the M/Vision Data Base. First of all, I want to make it clear that these gentlemen are not here to sell us M/Vision, nor are they here to convince us that we should buy because MSFC has already bought M/Vision. I have asked them not to take the approach of salesmanship, but rather to explain since we have already bought it. I spent a great deal of time talking Mr. Curt Loomis who is out of Colorado. He is the M/Vision Sales Manager. He has asked me a lot of really good questions to try to understand the scope of our group and what we are interested in so that he can tailor his presentation today to fit our needs. Do keep in mind that Marshall has already bought it. We want to look at this as far as how we can support this data base if we are to use it. This presentation is going to consist of roughly two parts. I asked them to give a basic overview of M/Vision. The second part of the presentation will be a demonstration at the back of the

room. I am going to turn it over to Curt Loomis and he is going to introduce the people he has brought with him.

Loomis Thanks, Cindy. I would like to introduce a few members of our team that you will talking with later today. This is Todd McClain and he is a sales person out of our Dallas office and handles this area and on the left is Ken Walker. Ken is the applications support manager for the western part of the U.S. and is also based in Dallas. He will be doing the demonstration for us. We also have Greg Crose who is one of the founding members of PDA and he is here also. Some of you may know him from previous meetings.

I want to find out how many of you have heard of M/Vision before this meeting. About half the room. One of the ways to best understand M/Vision is to understand its history. How did it come about? This history will tell you a lot about the product. First of all, for those of you who may not know about PDA, we were incorporated in 1972 as engineering service firm to the DOD. A lot of work was focused on doing finite element analysis, thermal studies, and characterizing and developing composite materials, carbon-carbon and carbon-phenolic materials. One of the things that we found in a lot of our finite element analysis work is that some of our analysis was being compromised because we didn't have good material property data. We determined that this was something that we needed to fix. As Ken just mentioned, one of the problems is that there

is lots of data out there, but you don't know where it is because it is not catalogued in any particular way. In 1982 we started an IR&D program where we developed the very first version of M/Vision for internal use. We used that over the next number of years with some projects that we had with the Air Force and then in the late 1980s we came out with a prototype because we decided that we wanted to come to market with a Material Software System. First of all we talked to some people like John Rumble at NIST and asked him for his feedback as to what would be required in a Material Software System. The prototype was taken out to 16 different companies for a peer review and we learned a lot. As a result of the peer review, we actually pulled the product back and rewrote it from scratch because there were some things we wanted to add. We didn't want a data base out there that was just the same as whatever ORACLE or some other RDBMS could offer. We wanted a system geared to, and specifically designed for, the materials engineering process. As a result of that, in August of 1990 we shipped our very first system to Aerojet and since then we have added some standard data bases to the system. Some of the data bases include the MIL-5 Handbook. We are contracted with Battelle Memorial Institute who is the secretariat for MIL-5. They actually keep the data base up to date for us and verify the quality of the data. One of the nice things about having data bases in electronic format, we are actually able to come out with new versions electronically, almost before it is published in a paper format. Some of the other data bases more interesting to this group are the PMC90 data base and we work

with the University of Dayton Research Institute and Dr. Robert Askins. They update the PMC 90 data base for us and keep that in order. We also have a MIL-17 data base that is available. The MIL-5, PMC 90 and MIL-17 and all of those data bases are validated data bases. Recently in the last year, we have come out with a new data base called the Producer's Databank. This product has over 17,000 materials from over 300 different manufacturers and this is just producers' data. A lot of customers want to search very quickly and find some information that is important to them. As a result of the work that we have done with M/Vision, there has been a tremendous acceptance because there is no other product out there like it. We have over 30 installations and some of them that may be of interest to you are: The Aerospace Corporation, Aerojet, Rocketdyne will have it shortly. On the F22 project, Boeing has it. Lockheed has it. NASA, at Marshall, Langley and Lewis have M/Vision. It is a growing list and it is growing very quickly.

In looking at how to present M/Vision to you, rather than give you a bunch of stats about the product, we wanted to take you through how one customer looked at deciding in what they needed in a materials software system. How they went about looking for one and how they are actually implementing it. The next number of slides have all come from NASA Marshall. Jimmy Lee in the STME group have shared these with me and we will talk about M/Vision in this way.

The STME, for those of you who don't know, is the Space Transportation Main Engine. It is a program under the National Launch System at NASA-Marshall. The STME has a team formed of contractors including Pratt and Whitney, Rocketdyne and Aerojet that are trying to develop this engine. One of the things that they decided that they wanted to do early on was that they needed a materials data base. This was based on some work that had been done in the past with the space shuttle main engine. They knew that they had some problems in the past in collecting information so they wanted to do it in the future, plus as new programs come on line after this, they wanted to have that information available so it could be used in newer projects.

They wanted to capture the material property data electronically and have it online so that it could be used as part of the design process. In the beginning they went through a QFE processed where they prioritized their technical requirements and then they went out and evaluated some of the data base architectures that were available today. One of the systems that they looked at using was the Materials and Processes Technical Information System that is at NASA-Marshall run by John Davis. That is based on an ORACLE data base. They found that there were some functional requirements that they had that that system couldn't handle. They did a second QFE process. They formed an agency team to come up with the types of data that they wanted to store, including the standard and pertinent mechanical properties and specific pedigree

information. They started out on the process of looking for a materials system. They went to John Rumble and he pointed them to PDA and M/Vision.

In the beginning it didn't quite meet their requirements, but we were very willing to work with them because we wanted to see what new functionality would be required. We worked with them and added some new functionality and they went forward to buy the system at NASA-Marshall.

Some of the reasons that they picked it was that there was capability such as the spreadsheet functionality to actually go in and manipulate the data. You don't find that in a normal relational data base like ORACLE. There is the ability to store raster or graphic images, CT scans if you will, things like that. There is the ability to store curve information. Any information that you have in the spreadsheet, stress strain curves, you can pull up and instantly plot a X,Y plot. It is really more than a data base. It is a Materials Software System.

Another thing that they have been doing as part of the group is putting together different data bases. In fact, although Marshall is just taking training on the system now, officially, Aerojet has had the system for a couple of years and Aerojet and Rocketdyne and Pratt and Whitney have been working on the data that is actually going into the system. It is pretty well defined.

Lutz What platform does this thing call for?

Loomis This system runs right now on what I would call engineering work stations such as a VAX mainframe, but it will run on Apollo, Sun, SGI, HP and IBM R6000. Most of our customers in materials departments don't have that hardware. One of the key things, the way most people use it is in an X Windows environment. Some of you may not know what X Windows and X terminals are. That is the ability to have the VAX as a mainframe and if you have an Ethernet or some sort of network off of that, you can actually configure your PC or MacIntosh to be a terminal right off of your mainframe. In fact that is how NASA-Marshall is doing it. They have MacIntosh terminals that will be tied to a VAX system. That is the way most of our customers are using it. You would have a central point and you really think of that computer as a file server where all the data is being stored.

Drake That is the same way we use it at Aerospace.

Loomis Some of the data bases that they have defined include low cycle fatigue, high cycle fatigue and tensile strength. Those are some of the data bases that they have started to outline and put together.

I think the usage is real important because this is what will decide for you what M/Vision can really do. They really wanted to track the pedigree of the material information so that there wouldn't be any controversy over what properties were used in the analysis. Capturing that pedigree was one of the reasons we rewrote the data base from scratch originally. One of the things that we added into the data base was what we call metadata, for those of you that don't know it, is data about data. All the data that you would want to reference can be stored in the system as a sublevel. That is one of the key things that we rewrote. Metadata allows you to track the pedigree information.

The next thing was that the group wanted the raw data in the system, so that each of the team members could go in and do specialized studies if they wanted to. I have talked a little bit about the spreadsheet functionality. That is very nice because it has all of the engineering equations that you wouldn't normally find in an EXCEL or LOTUS. Also the engineering spreadsheet can go out and call FORTRAN or C programs that you may have written where you may have a special code that you have developed that does synthesis or characterization of the composite material. You can do any sort of mathematical manipulations that you want to right there. And after you have done that analysis, then you can plot up the stress strain curves and see that instantly. That was real important to the group.

The next thing they wanted was to simplify the data reduction process and have a traceable path on how the data was reduced. If you have done some reduction, how did you go from here and get to there. One of the things that the system does is through the spreadsheet, you can easily see how the information was reduced and also the raw data stored right there along with the reduced data. You can correlate the information.

Another reason we rewrote the data base at that time is that we wanted to have excellent precision in the data base. If you have 60 units, is it 60 KSI and what is the precision? Is it $60 \text{ KSI} \pm 1$ and so in our system, we have the ability to go from 1 unit system to another unit system. And it carries the full precision along with that as you do that conversion. Ken will demonstrate that for you a little later.

The last point here is they wanted to be able to take out the material property information and they wanted to be able to take it out via the Initial Graphics Exchange Specification. It is a geometric capability to describe computer models of parts that allows you to transfer CAD drawings from one system to another system. They wanted to be able to input that data so that designers using CAD systems could use the material property data.

Another thing that has been helpful to PDA is the next step beyond IGES which is called Product Data Exchange Specification. What is happening is that the DOD and NIST are trying to develop a standard so that when somebody develops a part, they can pass not only the geometric model to somebody else who might need it, but all the information about the process. How it was processed, what materials, all that information. PDA has recently been asked to write that materials portion of the specification and we feel that was a good ratification of PDES' comfort level with what we are doing.

They wanted to do data exchange between the contractors and NASA-Marshall. Because you have a team, it is very important to have a concurrent engineering process that is as smooth as possible. They wanted to have common materials data and they wanted to eliminate test duplication. The next thing is that all of the data is there for you, the pedigree of the information is there. You have the raw data and the reduced data, any of the curves, any of the raster images from CT scans or microphotographs. It is all there for you.

The last thing was it allowed for easy identification of those materials that were not characterized. You could go into the system and do a query and find out what information is missing. If it is missing, you can actually synthesize those properties if you want to.

There were three other reasons that they picked M/Vision that were very important to the whole process. These really separate M/Vision from the other materials data bases that are out there. One of them that we talked about before was the ability to store raster images. We can actually go in and do limited image analysis. We can go in and do histograms and density studies. We'll do some of that for you in the back here. Another thing that was very important was the ease of use. Most of M/Vision has an easy to use motif interface. What motif is, is a standard that sits on top of the X Windows and it is much like an Apple MacIntosh. It has pull-down menus and click-on boxes. You just highlight something and it goes into the box. Most of M/Vision is set up that way and the parts that aren't will be in the next release. There is one more thing that made this system unique. There are two ways to access data. One way is it has a hierarchical data interface. Think of it as an inverted tree. When you want to get information, you come down to different branches of the tree to get to the data that you want. That can be very fast if you know specifically what you are looking for. On the other side you have what is known as a traditional relational data base management system like ORACLE. With a relational system, you may not know in advance what information you want. You may want to come up with a question and the system will come back with just that material. You can do "what if" questions. M/Vision gives you a view on the data in both ways.

Lutz Is M/Vision user configurable or does it come as a package from the company?

Loomis What you have is 32 different levels that you can put the data into and in our training class what we typically do is spend a day just define your own scheme. For the training class, we tell people, " if you have a data base in EXCEL or some other format, we can read it into our spreadsheet". From there it is inserted into M/VISION.

PDA has just come out with a new product that is interesting and unique. We have a finite element analysis and modeling program call PATRAN3. We have developed a module called P3 Materials Selector and it allows people to grab any property data that is in your own custom data base or any of the standard data bases that we offer.

This is a worksheet that was given to me by Bob Jewett at Rocketdyne and this some of the data that they are going to be inputting into the system. This is just a form that they use. They could actually use an EXCEL spreadsheet to collect the data if you want and then feed it into M/Vision.

This is some tensile data that they are going to be capturing and this is the scheme that they have come up with. There are the materials, the specimen, the environment, and the properties.

To have this work across multiple organizations, you need an infrastructure. You need computers, communications and local area networks. All of the different team members are tied into Marshall and will be able to access the master data base that will be there.

To summarize, how can a materials software system help you? It can allow you, by cataloguing information, to eliminate multiple tests in a test lab. You simplify the process of data reduction. You speed the process of developing your design allowables. Most importantly, you capture the pedigree information. You have online access to standards and producers data. You have qualified material properties that are available to be used by the analysis and design people. Finally it is an enabler for concurrent engineering. Concurrent engineering is essentially having different groups simultaneously involved in the process of designing a product so that you get there faster. The major design decisions have been addressed up front so that you don't have more costs and longer lead time on the back end. That is the presentation of M/Vision.

Mills How much carbon-phenolic data do you have in it right now?

McClain None in the product that we sell to you.

Mills You are selling me this to put my data into your format.

McClain We are working toward bringing carbon-phenolic data into this format for a project for Hercules.

Loomis What we are finding in the composites area is that most of our customers want to develop their own custom data bases. I would say that most of the customers that we have today, use the system to develop their own data base and then a lot of them will use the standard data bases that we have available. We are going to be adding more data bases as time goes on.

Mills Okay, but the point that you made a few minutes ago about eliminating some tests done by different agencies is really, the key factor to that is a data base that is compiled that has NASA's work, my work, Hercules' work, Thiokol's work on a given product and that seems to be a major shortcoming, especially considering the cost per year of the system. What is the current cost per year? 30K?

Loomis If you purchase it up front, it is 30K. That is with all the data banks, everything. M/Vision, to lease it for 1 year is \$9,000. The MIL5 Handbook is \$4,000.

Mills That gets you no data base except the MIL5 Handbook.

Loomis Right. The other two are \$2500 a piece.

Mills Are those maintained if you pay the \$2500 per year?

Loomis Absolutely. Or you can purchase it paid up. The payback point here is about two and one-half years. If you know you are going to using the system for about two and one-half years, some people will purchase it up front.

Lutz Is the 30K include training and subsequent updates to the software or is the 30K just for the software package?

Loomis The 30K is when you go and buy not only M/Vision, but the three standard packages. There is another \$2000 fee if you want to go to the training class and it gives you two people in training or we come out and do customized training onsite. Then from there, if you purchase the package, there is a maintenance fee to get updates. If you lease the package, maintenance is included for that year period of time automatically.

Mills What is the yearly fee for maintenance?

Loomis It is 16%. Most software is anywhere from 10 to 20%. We are 16%.

Drake 16% of what?

Loomis Of the purchase price. An important point to bring out is that we will be coming out with a view only copy of the data base at a much lower price. Let's go on to the demonstration.

Upton We need to document all our specific areas of interest in cured materials testing. We don't really want to get bogged down in a lot regulations and all. We want this to be our output to the industry. One of the things would be an SPIP document on cured materials testing. Eric has taken a lot time to look at this. He has looked into what is being done now. He has given out a survey that unfortunately I got the cover letter on so quickly, I forgot to give Eric credit. The survey that so many of you have returned to me today, the survey came from Eric. I do have blanks, so please, if you are cognizant of cured materials testing, fill out one of these surveys. Your information is going to help us out a lot in putting together what we are doing. Eric is going to come now and talk about his latest work in this area. Meanwhile, I am going to circulate these. Eric.

Stokes I think there is fairly good agreement in our community that existing carbon phenolic acceptance tests for cured materials are of limited value. What Southern Research has been asked to do is come up with a process which will result in a selection of a new set of improved carbon phenolic acceptance tests. Rather than go out and just do this on our own, we want to involve the community in this

process. What I would like to do is go through how we think the process should look.

The first part in this process is agreement amongst the community on the desirable properties of acceptance testing. Once we have done that, then we would like you to rank the properties based on desirability. Our feeling is that the most desirable property of an acceptance test should be a predictor of the failure mode or performance. However, if this is not the case, we can always modify the process given that predictor of performance is deemed the most important quality of an acceptance test, we would like input with respect to which material characteristics govern the key materials events. Following this step we plan to take these lists and combine them and come up with a consensus among the community on which material characteristics are governing the key material events. At that point, we will then look at the material characteristics that we are interested in and try to choose tests that will give us information about these material characteristics. Again this will be done with the community in a survey form. Again, we will come to some sort of consensus on which tests we think can cover most of the properties that we want to look at and we will select a test.

Drake You have up there a predictor of the failure mode. I think I would be more interested in a predictor of the success mode.

Stokes What I would like for you to do now is take that first survey fill it out. Surve
One lists the properties and acceptance tests that we thought were important. I
am sure there are additional properties that you might have that you might want
to write down. I would like for you to complete the survey at this time. Go
ahead and start working on that and then we will collect them and Cindy can
tabulate the results. This survey is needed for the next part. There will be a sort
of a delay here, but to expedite this process, we need to get all these first surveys
in.

Hill Hey, Eric, I have a question. What do you mean by precision, by accurate?

Stokes Precision is the amount of test variability. Accuracy is how close the average
data comes to the actual value. For instance, you could have a value that was
20% off from the actual value, but if the repeated test gave you that same value,
it would be a very precise test.

Croese Elaborate on sensity.

Stokes There are many definitions. I prefer not to define it in my terms.

Croese A test generally produces a number and the number might range very widely and
yet the performance not be much different from one extreme to another. That is

one extreme. Another extreme is that what you are measuring only changes a little bit numerically, but that little change has a big change in how the part performs.

Stokes It would be the second one, because what you are talking about are properties of the test, not the material. Is the test sensitive enough to pick up the differences that are significant.

Croese So the second would be a picture of the undesirable?

Singer Do you mean significant or relative?

Stokes He is saying if there is a very small change in the property, but that very small change is very significant to the performance. Can the test pick up that very small change?

Singer Have you identified the variables that are significant?

Stokes That is part of the third survey.

Croese I don't know whether to answer desirable or non-desirable.

Mills Are you trying to get one parameter that will be your acceptance parameter regardless of whether it is an exit cone, or will it be different for each component?

Stokes That is a point to be made.

Mills Typically, what I do is try to relate to some data base and say I have always been within these parameters and as long as I don't fall outside of those parameters doing a room temperature test. I set myself up as being the same as what I qualified. I don't generally have the luxury of being able to adjust an exit cone which may be interlaminar shear. What you are saying is that there will be a separate acceptance test for each part. One of the things I am trying to do is create a large enough data base by doing the same test, the same orientation from a number of components to determine if I fall outside the range.

Lin Eric, what is the difference in material property and other desirable properties?

Stokes Other desirable properties like machinability, or susceptibility to damage in transport, or something like that.

L.Johnson What is a material property then?

Stokes For instance, the residual volatiles test is not a material property.

Beckley It is or it isn't.

Stokes It is not. It may be desirable to generate a large material property data base to use for other things besides just acceptance.

Singer I am very much interested in having an indicator that tells how a particular material will respond in the environment that I am paid to deal with. If that can be used for six other things that some other person is paid to deal with, I don't really care. Let him pay for it.

Stokes There maybe somebody above you that has to make that decision. There is somebody out there that is concerned with both of these situations.

Singer I work in an office where the guy above me asks me what to do, so if your boss doesn't care what you are doing as long as you produce revenue, fine.

Stokes Let's go on to the second survey. In this case we want to show relative rank of the importance of these various characteristics. Cindy has taken that other category, additional properties and tabulated the results. I am going to put these

results up here. You can just put a letter down on your survey and give it some sort of rank.

Lutz If a test isn't accurate or precise, is it really a properties you want to run?

Stokes Obviously, some of these tests are desirable.

Lutz That is what I am saying. It is not a judgement. It is a requirement.

Stokes Sure.

Lutz Then you can't really rank it.

Pinoli Do we give that yes or no rank?

Stokes Do it however you want and we will sort it out later.

Bhe Eric, are the mechanical properties included in the material properties?

Stokes Yes. What we are saying there is that is it desirable to have a test that will give you a material property, whether it is mechanical, thermal, or whatever.

I guess the next thing that I need to ask is if there is any disagreement that predictor of performance is the primary property that is of interest in an acceptance test.

Lutz That is assuming you can identify the failure mode.

Croze I put a different one. I put relevant to performance. That is slightly different to predictor of a failure of mode.

Stokes Okay.

Croze I changed it because I with the predictor of a failure mode, it might cause us to overlook some things that we don't have some direct evidence of, that we only have the indirect evidence of like statistical analysis and so on, that shows a close correlation when you put the physics to it.

Stokes I am not following you, Greg.

Croze Well, although we probably proved that it is not the case, that a possibility might have been our volatile contents.

Stokes Might have been a variable responsible for some things.

- Croze In other words, the performance might vary with the volatile content. We have grown up to see that life is not that simple. but maybe there is something else.
- Stokes Something else beside predictor of failure mode.
- Croze Some other property that correlates with performance that we don't have a good physical explanation on.
- Ma He is talking about optimizing performance.
- Coffee The distinction that we ought to be making because this is labeled acceptance test, go or no go. Keep it or throw it out. The distinction I made when I filled out on that last item, material property, was I may not reject the material, but I kind of want to know it because I may adjust my process variables while I am using the material.
- Stokes It is still not clear in my head, the distinction between predictor of failure mode and part performance.
- Beckley What about an erosion rate that is not a failing erosion rate, but you don't really like it to be 6 mils per second.

- Stokes Okay. If you define that then I call that a failure mode. I guess we should take the word failure out because it seems to mean something catastrophic. Predictor of undesirable performance. How is that?
- Croze I think that is a better way of saying it and it brings it closer to the point that I was making.
- Lutz That doesn't require you to know what the mode is.
- Mills Generically, would you assume that you would have as many tests as you have failure modes?
- Stokes Not necessarily.
- Singer Is the test that correlates with three failure modes is more desirable than one that doesn't correlate with any failure mode? Is the test that does not correlate with any failure modes useless?
- Stokes Maybe. Can we agree that performance is an important issue here? You need to list to the best of your ability those material properties or cured material governing these events, these being the primary undesirable events that may occur

in a nozzle environment. The primary factors are those that we think of as most driving those events.

Lutz I would like to make a comment. Two things. Material properties that govern the following key material events, a lot of these cases, it is the processing parameters and design that affect these events, rather than material properties. You are also making an assumption that you know or our opinions are going to tell you what governs these events and you are going to base tests from that. I think that is not a street you want to go down. Another thing is, you are going to run tests that are going to determine whether these events are going to take place, assuming a static environment, when what you are testing for is happening in an environment where you have heating rates that you can't duplicate in that testing.

Stokes We are not trying to duplicate failure events as an acceptance test. We are trying to find properties of material that will tell us whether the event will occur.

Lutz I haven't seen anything definitive presented that tells me what, for instance, Elkton's designs don't have ply-lift. We don't have pocketing. We don't have a number of these things. That relates to the design of the process not the material property.

- Stokes The design of the part has to do with material properties. The constituent properties and processing governs the material property. We have the cured phenolic material here and we have to see whether it is going to have some anomalous behavior.
- Lutz You can take shuttle material cured by shuttle practices that is, for instance, if ply lift is going to occur and take that same material and made by the same process, but with a different ply angle, ply lift will probably not occur.
- Stokes You must have a correlation between what values of that material property are going to cause the anomalous event to occur.
- Lutz That is what I am saying. You can have the same properties as shuttle material and put in a different ply angle...
- Singer You said a few minutes ago that there is a material property that governs ply lift and that is the error in your thinking.
- Stokes It is not an error in my thinking, but an error in the expression of my thinking. I realize there are more than one material characteristics for some of these. That is why there are many lines on that survey.

Singer The lines on that survey are inadequate to describe the number of factors that are relative to ply-lift.

Stokes Rather than try to inhibit this process, I would like to get through this first stage as best we can. I realize there is a lot of controversy around what causes these events to occur and maybe even this process of selection of new acceptance tests. If we can get through this first hurdle, maybe we can put something together that will tell us how successful we have been or modify and do something else later.

Lutz I guess what I am saying, you are testing for properties that exist in a static environment when the properties that the nozzle has in a dynamic environment don't relate at all.

Stokes That's right, but there are things that you can test in a static environment that will indicate whether that anomalous event will occur.

Singer That is a marvelous statement to make, but to demonstrate it.

Stokes You have to understand the relationship between material characteristics and the process. I understand that there is not good agreement on what causes these events to occur.

Singer We have to understand that relationship because we are designing parts and you are trying to design a test program to evaluate them and you have to understand the relationship in order to do that and there is no demonstration yet that you have done that and there is not in the questions.

Lutz We wouldn't be here if we knew why all these things occurred.

Singer We don't know the answers.

Stokes You know the answers to some of them. You know why erosion rate is greater in some environments than others. The same is true for char depth. We pretty much know why pocketing occurs also.

Beckley Even when it pocketed the characteristics didn't differ that we know of, did it? That is the worst part I can think of and this is a fixed design and a fixed use and many parts fired satisfactorily. We get one part that didn't fire well. Was it a material characteristic or was it a process characteristics and within the part did we find anything that absolutely said it caused pocketing.

Stokes It is true, we have not fully proved this. We haven't gone back. You have to go back and remanufacture a part and demonstrate that the failure event occurred because of the change in the identified variable.

Singer How much of the answer do you think you have?

Stokes Because this part of the puzzle is missing, we are going to try to do the best we can with what we have. New findings may come to light on down stream which may warrant the choice of additional acceptance tests. We have to do the best we can with what we have at this time.

Mills I think this is a very desirable goal, but I don't see that it is practical unless you have demonstrated that factor A caused a failure. But to test factor A on faith is not a lot better off than we are right now.

Stokes I guess we need to go back a step then. We need to decide, what do want an acceptance test to do. I thought we had set this, that we wanted an acceptance test to tell us whether we are going to have problems.

Drake An acceptance test is to predict lot to lot or part to part variability. What it will do in the intended function is yet to be seen.

Lutz If you know why these things occur, you incorporate them back into design and your process. You don't test for it at the end. What happens if you have a variation in that process that throws you off.

- Singer Then it won't comply with what you qualified. You ought to throw it away.
- Mills You have really violated your agreement with the government that you are going to qualify what you fly. If you are really outside that envelop because you have done something really change.....
- Stokes Do we know all the process material variables that govern this? Do we know at the prepreg level, the carbonized level, the factors that affect this?
- Beckley They are set up in their own acceptance tests as well. They have met the gates and they move it to the next step. You pass through those gates and move it on through to cured component. It has a set of acceptance tests as it passes those gates. All those things were combined beforehand into the design, development and qual program and said if you meet all these gates, low an behold it did work.
- Stokes Why are we falling out of this regime?
- Beckley In that same cone, there were thousands of square inches that did not ply lift in the same cone.
- Stokes There are some cones where 95% of the cone lifted.

Lutz Because the ply angle was wrong and the cure practice was improper.

Stokes Instead of going round and round, let's do the best job that we can on these surveys and move on. We can come back next time and get into this again.

Upton We can have off line discussions but we really do need to make some progress here on what we can do now.

Thomas I think they need to consider more than material properties.

Stokes For a fixed design, it is material properties.

Thomas We have had too many exit cones that didn't ply-lift. We have only 3 out of several hundred that ply-lifted. It was a processing problem. Those that ply-lifted had had DRs written against them.

Stokes However we don't know what happens up there, because we don't get the exit cone back.

Thomas It doesn't matter. There wasn't a factor of safety in the flight. The exit cones performed the job they were supposed to. We have had 50 some odd flights now.

Crose Did the 404 rings that pocketed on the STS8A , or whatever, some years ago, did they pass acceptance testing?

Thomas It passed everything except there was vacuum bag rupture and cure cycle variation. That was outside the spec. That part was sold on a DR, discrepancy report. A processing discrepancy.

Crose So it failed acceptance. They just went on and used it.

Thomas They didn't go on and use it. It was processed through the system on a DR and used as is because it fell outside the spec.

Mills It is not uncommon to buy something like that for a static firing.

Thomas That is why these that had DRs on the exit cones were identified for static tests only. They ply-lifted.

L. Johnson Another thing about the survey in general. You have a lot of different people in here with a lot of different points of view. You may have ten people with the same point of view and forty of another. That is going to weight your survey.

Stokes We are not going to weight these.

Upton This is just an information gathering tool. You may disagree with what he is asking, but he has a specific reason in mind for asking this particular set of information. This is not to say that we are going to set up a test plan and implement it because of this survey. Can we just approach it as such and move on. Interested parties talk to Eric about it later. We are just trying to start something. A lot of people I have talked have said that we have a problems with inhouse cured materials testing. Eric is just sort of do a check on current conditions and see what people are doing now or what they think. It is really not designed to get into all this now. It is just a materials requirement now. Can we just let Eric continue for now and hold the questions for later?

Stokes Finally, I would like to review our (SRI) view of what material characteristics are responsible for the key anomalous events observed in RSRM materials. This This will help jog the memories of those not intimately familiar with these events. These are properties that result in a higher susceptibility to excessive erosion rates. Examples of when that event was observed are shown here.

Char depth is the heat affected region within the part after completion of firing and is represented by the dashed line there. Some of the properties that result in a higher susceptibility are higher thermal conductivity and lower heat to pyrolysis.

Pocketing is thought to occur when you have a material restrained in the cross ply direction and the plies are aligned 90° to the flame surface. You go through a pore pressure induced high thermal expansion that puts an internal tensile stress on the fibers causing fiber breakage. Once the fibers break the material is severely weakened and pockets readily.

Ply-lift, multiple cross-ply failure of the material that usually occurs at 1 isotherm and has been shown to occur at the intersection of the vapor pressure curve and the across ply tensile strength of the materials. This indicates the event is moisture driven and occurs below pyrolysis temperatures.

Properties that affect this are low temperature permeability, lower across ply tensile strength, higher vols content, and possibly low moisture content.

Singer Measure how?

Stokes Delamination is thought to occur because of the large across ply thermal contraction that occurs at elevated temperatures. The lower temperature material holds the material in place.

This thermal structural failure has not been shown to occur in carbon-phenolic but it has been seen in carbon-carbon and again it is the result of thermal expansion.

In this case higher yarn expansion, lower yarn strength and high yarn modulus drive the event.

Finally wedge out is thought to be pore pressure related. The across ply compressive stress driven by pore pressure in a material that is not 90 or 0 degree aligned, results in a shear force component in the material that causes an interlaminar failure of the material. The failed material is then no longer attached to the part and small bending movements result in large inplane stresses the yarn.

Thomas That usually only happens in the short plies.

Stokes Again, higher across thermal expansion, lower permeability and lower interlaminar shear strength.

Finally this table summarizes the various events and breaks them down into what we consider primary factors and secondary factors.

If you cannot complete the surveys at this time, I would like to get the surveys back by the end of May.

Upton Okay, thanks Eric. We just have one more thing on the agenda. It is something relatively new for our committee. Some of you who are familiar with SPIP, you

know that the 3.1 area is concerned with computer modeling and such and Dr. Greg Crose is a representative on that side as well as our group. What happened was, the people in the committee were talking about the need for the computer modeler from an engineering standpoint and it so happens that Bob Bunker and Thiokol does do a lot of computer modeling work. Greg and Bob have provided a presentation for us today. bob is going to start and he is basically going to speak on the engineering needs for computer modeling and the Greg will present to you, too.

Bunker Thiokol has had some TQM classes and in one of those classes, they have a video tape that tells about paradigm. I didn't know anything about paradigms until then, but what it is that you take data and you interpret it based on how you view the world. For instance, if there are some data that doesn't fit the way you view the world, you can either ignore the data or change your paradigms to include that data.

Beckley You file the data as I don't believe it, but I won't discount it.

Bunker Right.

Beckley You sort until it proves to be true.

Bunker

Right.

Andrew Prince and myself and Tim Lawrence of Marshall wrote a paper a couple of years ago. We had some 5055 samples that came from a nozzle part. We conditioned another some samples in 100% humidity, 100° for about a year. Another set of samples were in a dry environment for about a year when we put them in. There were some surprising results. We put them in a torch test and all the samples which were conditioned in the wet environment didn't pocket and all of the dry samples that we tested pocketed. That is the exact reverse of what we thought would happen. I didn't believe it and I thought he had switched the samples, so I had him do the test again and we got the same results. I hope that we can keep that in mind and change our paradigm because I think everyone is kind of ignoring the data, and looking at constituent testing as to why materials perform the way they do.

I would bet \$20 that if you took a 5055 ring and put it in a moisture environment and one in a dry environment and fired it in a 40 lb. charge motor, that you would see the same results. I would like to see that test. That is not the topic of my discussion, but it is related.

Generally, it has been thought by most engineers that material properties depend upon one state, the thermal state. In fact, most of the thermal codes and

structural codes, only have the properties as a function of temperature. In reality, they are probably a function of several states, especially materials like carbon-phenolic. You may not refer to these as actual states, but for the purpose of this presentation, I am calling them states, the thermal state, the chemical state, the stress and strain state, moisture content and the porosity. I think when we design computer models, we ought to make the properties as a function of all these states rather than just one single one. In the past the thermal codes have accepted properties as a function of the thermal state and the chemical state, to some extent. Some of them have. Not most of them, but some of them. Maybe some of the structural codes have, too. I am not sure. I don't think they have, but maybe Greg can shed some light on that. Anyway, we are in the process of developing codes that make the properties as a function of all these states. In the same light, in lab testing, the material properties have to be based upon, not just the thermal state, but the chemical state, pore pressure, and so on.

These are some of the properties that need to be evaluated based upon those states. It may or may not be all of them, probably not. This is the way you compute the thermal state and you will notice that it has a conduction term, a storage term, and a generation term. This is the thermal state.

The chemical state is generally defined by an Arrhenius equation. The i means that there is a chemical reaction. You can define it by several different chemical reactions, not just necessarily one.

Bhe Bob, what is the v in the chemical state?

Bunker The degree of chemical reaction, the degree of completion is what it is. For instance, we generally model in three different components, three different chemical reactions, and that is the degree of chemical reaction. More than three or less than three or whatever you want to do.

The moisture state can be defined as another diffusion problem in these type of equations, very similar to the thermal. Generally you don't have to do this moisture calculation. It is a performance calculation. In other words, how is a nozzle going to perform doesn't depend on the moisture diffusion rate because the moisture diffusion is so slow that the only time you have to model it is when you are doing modeling for the processing, of making the part. You may want to use that in the evaluation of the performance. You may not know how much moisture you have in there and that is probably very important. Then when it comes off in the pyrolysis gas, you may want to model it in the zero order of reaction.

Pore pressure, you do have to model it. It comes off as the resin decomposes and so you have to model that and it is something that you have to track throughout the calculation. Generally in the pore pressure and the temperature calculations, your time spans are so small that the previous temperature and the previous time span and the previous pressure can be used as a basis to determine the properties for the next one, because they are not much different than the current temperature and pressure.

Stress and strain, maybe you don't need to evaluate that in the order of seconds, maybe even tens of seconds. Greg will know more about that. Nevertheless, you have to track all of these in the analysis.

Most of these examples come from SORI by the way. These will show how the properties are a function of these different states and not just the thermal state. This shows a stress strain curves for a difference of heating rates, 2° 10° , or 3° and 10° per second. This is how many seconds it was held before the test. You can see the difference there of the 2° versus the 10° and of course what that really is is probably the property based upon its chemical state. If you have a good relationship, you can compute what the chemical state is. One of these is a 120 second hold and one is no hold. The other is a different loading, but I think all of these are because of that chemical state. In other words, the time temperature relationship is all different for every one of the those. This is a real

char of a 5055. I don't know how close the Arrhenius equation that we are currently using is, but it is probably pretty reasonable. It shows you how char changes with the different heating rates. A lot of times we put in the property as a function of the heating rate and that is not a true description because at one particular point, the heating rate changes. This came out in an analysis that we did on an exit cone and the distance down, say about $\frac{3}{8}$ " below the surface, how the heating rate changes during the firing. You can see it goes all the way from 0 to 100° per second. This is elastic modulus and it is really a function of the chemical state.

Drake Is that in thousands of degrees?

Bunker Yea, so in other words, 0.6 is 600°. I think there are a couple of things we can get out of here. One is that probably the effects of the moisture content, the moisture state and the other the pore pressure, I believe. For instance, you can see that you have two different diameters, $\frac{1}{4}$ and $\frac{1}{2}$, and see the different responses of the thermal strain. That is probably the pathway to internal pore pressure. You can see how pore pressure effects thermal state. The heating rate gives you an idea of how the chemical state is and the size is an indication of how pore pressure is.

Let's go back to the conclusions. Properties should be based as a function of all these states we have talked about, not just the thermal state, as has been the case. Another thing that will give you some insight into how to interpret lab tests is to model the tests themselves. If you have good models for your chemical equations, you can tell the chemical state. Another thing is like the RTG, you can run that through the thermal history to determine the chemical state and possibly the pore pressure and calculate that and better interpret the results. The other thing is, I was thinking that we would not only be able to calculate the states, but you could even make some measurements. For instance, maybe if you are doing stress strain curve at temperature, maybe you measure the electrical conductivity to get an idea of what the chemical state is from a measurement standpoint as well as a calculation. These are just ideas that might be tried. I don't know if they will work. Then relate the electrical conductivity to the state by measuring the conductivity by TGA or DSC so that you can have a correlation. That may or may not be able to be done, because in TGA you generally burn it up. These are just ideas and I am going to leave it Greg to go on.

Upton Thank you Bob.

Croese I don't disagree with anything Bob has said and I am intrigued with his ideas about electrical conductivity. Today, I would like to try to get you to see the

problems that we are all talking about through the eyes of the analyst or the designer. In this 1st viewgraph, I am trying to give a global view of rocket nozzle analysis. Traditionally there are three fields involved, aerodynamics, thermal, and structural. Each field kind of stay away from the other and do their own thing and there is a small amount of communication. The dashed line represents the problems that are unique to carbon-phenolic or other ablative materials. For carbon-carbon we are pretty well satisfied with the autonomous situation. With respect the ablative materials, though, we have to consider the pyrolysis event and when we do, it couples all the disciplines together in one big family. What we are doing in the SPIP Task 3.1 area is trying to develop tools and methods that address the fact that all this couples together. For example, in the pyrolysis event, there is a coupling of the structural and the pyrolysis with respect to pore pressures that are developed and something like deformation dependent permeability as Eric eluded to earlier. In the thermal area, there is mass transport to be considered, heat of reaction, reaction rate, and so on. In the thermal area there may be deformation dependent conductivity that is facilitated somehow in pyrolysis. These are the kind of problems that we have to deal with. We must try to establish all those couplings between our codes, determine how codes must be written and develop the data to feed those codes.

Our focus is generally on the problem areas. We are concerned about the pocketing event, going back to the original STS 8A pocketing event where we had

anomalous erosion due to the pocketing. This cross section of an RTG test illustrates the pocketing failure mode. The nozzle section shows there is some more cracking at the base of the erosion pits. Here is the ply lift that we had, the separation of plies along an isotherm. We have this problem in the cowl area and in the aft exit cone of the nozzle. Also there are difficulties that we call wedge out where chunks of material fall out for one reason or another. Eric showed you a picture of that.

Now I am going to step backwards and show you analytical results using the conventional analysis that doesn't have all the couplings and so on. It does have some intelligence built into it with respect to how we model the material properties and how we use the material properties in the analysis. Basically, with respect to the pocketing event, we look at the strain in the fiber direction which we believe is associated with pocketing. The buildup of strain occurs around 800F. If you look at the strain to failure curve, you can see that the predicted strain is approaching failure at this point. This is the signal in that analysis that we have a situation where there might be a pocketing kind of failure.

If you look at the analysis that we do of an exit cone and you look at the across ply stress and search for some tension, what we find in the analysis is that in this temperature range where we think we have ply lift, we don't have any tension stresses. We do have interlaminar shear. Now pore pressures are additive to

tensile stress due to the resistance of them by low permeability of the solid phase of the material. The pore pressures really act to augment the tension stress and strain in the solid phase of the material. Therefore, there is actually some tension in the solid phase of the material even though conventional analyses don't reveal it.

If you look at across ply stress and interlaminar shear as an interaction curve and imagine that there is some failure curve that looks like this, you will see in the conventional analysis that we are predicting combinations of across ply tension and interlaminar shear that suggests that the material should be safe. If you add in the pore pressure influence, we can very easily visualize that the stresses are outside the failure envelope and that we have a potential for ply-lift. Therefore, even in the conventional kind of analysis, we have a qualitative signal for where you might have ply lift.

As we look at the nozzle and consider wedge out, we see a stress distribution in interlaminar shear stress that nearly reaches failure around 800F and starts to approach failure at around 2000F in the opposite direction and we approach failure again out near 3600 to 3800F from the other direction. Now in interpreting these analyses, I can replace temperature with distance along the ply. You can think of this as the distribution of stresses along the ply at any given point in time. You can also substitute a time scale for temperature and study this

as the history of stresses at a point as a function of time. It is not too hard to see that the cyclical stress would place quite a burden on the material. In those areas of the nozzle where you have this stress cycle, you frequently have a wedge out kind of condition at the ring edges.

To talk a little bit more about wedge out, what we discovered in doing our analysis is that when we get close to an interface between two rings, we find large cross-ply tension due to the pore pressure developed. This is sufficiently high to create an initiation event for across ply tension failure. So the initiation of across ply tension failure at once point along the ply creates a situation where, with the addition of some other mechanical event, a wedge of material can move away from the remaining material. This is most undesirable when it occurs during burn, although it frequently occurs at the end of burn.

If you look at the overall failure issues and then look at ply angle effects (what I am really talking about here is ply angle to an isotherm), you can see that at low ply angles you have stresses that correlate with ply lifting, at high angles you have stress that correlates with pocketing and at intermediate angles, we have shear stresses and across ply tension that may correlate with wedge out. There are regions of ply angles where we don't have critical stress predictors. In components designed with those angles, we seldom experience anomalous erosion

events. Therefore, there are probably optimum ply angles that can be chosen for design.

We have done quite a bit of sensitivity studies with our analyses and they have revealed some interesting points. We modeled the RSRM nozzle and looked at three areas, the exit cone, the throat and the entrance areas, and we varied the ply angle in different regions, etc. We have done a fairly complete sensitivity study and unified the results of those analyses. Let me mention one more thing. We did the thermal analysis with a thermal code that does account for pyrolysis. We did the analysis at various stations in a way that gives us temperature distributions that are highly accurate. They are much more accurate than any you could generally get out of a conventional 2D nozzle analysis. The results that we achieved are due to the fact that we did a very careful, high resolution modeling of the appropriate responses.

If we ignore the stress components that don't matter and look only at the stress components that do matter and their peak values in a given nozzle ring, every time we got almost the same across ply stress. The critical stress appears to be invariant with time. Part of that is probably due to subtleties that our conventional analysis doesn't really pick up. When you see analysis that suggests something different, it is probably because of the coarseness of the analytical approach, not the physics of the material being modeled or the design of the

nozzle. This is one of the most interesting results of the sensitivity analyses. If you plot a critical parameter such as maximum across ply stress as a function of ply angle from the nozzle axis, (this is the ply angle you deal with in the fabrication of a part), you get points all over the map. There is no correlation with ply angle. If you replot that information and look at the results of critical parameters versus ply angle measured to the heated surface of the material, or ply angle relative to the isotherm, everything falls in line. The next viewgraph shows strain in the fiber direction versus ply angle to the heated surface. The 90° ply angle is where the plies are perpendicular to the surface and the 0° ply angle is running parallel to the surface. What is interesting about this is how easily you could get away from being worried about pocketing by changing the ply angle from a high value to a slightly lower value.

In the next viewgraph, if you look at across ply stress versus ply angle, we are looking at a parameter that must have something to do with ply lift. Again we looked at all the different ply angles and a nice trend emerged. When the ply angle is parallel to the surface, we have the maximum. Note that these are all negative numbers. This curve needs to be augmented by pore pressure in order to see that actual stress is the solid. With ply lift you don't have as sharp a drop off as you do in pocketing, so it takes some substantial changes in ply angle to get away from ply lift by design.

In the next viewgraph, if you look at the stresses most critical to wedge out, consider the interlaminar shear stress versus the ply angle. This maximizes at a ply angle of fifty to fifty-five degrees. The allowables in shear are quite a bit lower than the prediction. That is a little bit uncomfortable. It probably means that during the burn, the ply has a shear stress enough to cause localized delamination that propagates with the critical isotherm. The char layer is probably full of material where at some point in the burn there has been a relative shear between the plies such that if you applied that shear stress to a large volume of material, you would see a gross failure. Remember that stress oscillates with time, so that with time, it shears in one direction and a little later it shears back in another direction. Whether that adds up to wedge out or not is a secondary event that is not modeled in conventional analysis.

The conclusions that we reached in the sensitivity study were that predicted char and erosion rates were greater in small motors than in large motors. there is very little difference in thermal behavior, upstream or down stream of the throat, and there is very little effect on nozzle size or heating rate. I say heating rate because even though the different positions in the nozzle experience different heating rates, the critical stress response is nearly the same. The major determinant of the critical stress levels is the angle of tape wrapping. Bob mentioned our paradigm. I have been describing a paradigm that doesn't involve some possible contradictions. Contradictions may occur due to coupling of the conductivity,

permeability, and deformation. In other words, fully coupled codes could show differences in these kinds of conclusions. For example, the path length for pyrolysis gas escape can change these conclusions. The pyrolysis gas flow from upstream pyrolyzing components would tend to cool down stream components. There are 3D phenomena that aren't included in these calculations and other local flow field disturbances around joints between the rings and the nozzle and so on.

Lin Greg, most people do not account for propagation of local damage.

Croese Obviously these analyses are assuming that there is no damage, so what happens after there is damage is not addressed.

In the Task 3.1 area, we have been working on pore pressure driven analysis to explicitly treat these pyrolysis problems in both the thermal codes and the structural codes. If you do that, what you have to face in the structural codes is the fact that pyrolysis gases form during burn and develop pressure against resistance to flow. We visualize the material has having a porosity through which gases must flow. Gas is generated and then flows out through the permeability of the material and in the process of doing that, pore pressure builds up and loads the material in a way that is similar to thermal stress. In conventional analysis, where we use specimen test data that includes pores pressures in it, it is really modeling it that way. It is just that we haven't distinguished between thermal

expansion and pore pressure induced deformation. Here now we seek to distinguish between these two parameters explicitly and quantitatively. There is a sort of a problem. The effective porosity is not equal to the volume porosity. What that means is that the area over which the gases act is not calculable from the porosity of the material. We treat the problem macroscopically, even though the events that are controlling things are microscopic in nature. It becomes highly coupled. Permeability is a function of the porosity. The flow is a function of the permeability and the mass generation rate. Pore pressure is a function of the flow field and the mass generation rate. The deformation is a function of the pore pressure and porosity is a function of deformation. All coupled up!

To do this type of analysis, you need a fully coupled code. In the conventional analysis, the stress is compressive in the area where pocketing can occur. If you account for the pore pressure explicitly and just look at what is happening in the solid phase of the material, then you see the tension response. By doing the pore pressure driven analysis, we can see the stress state that causes the anomalous events.

Similarly, in the exit cone where ply lift is a potential problem, when we do the conventional analysis, we see very little response in across ply tension. As soon

as we put the pore pressure in and threat it explicitly, we see the large across ply tensions that could be responsible for the ply lift.

As a way of concluding, based on our work, I have listed what I think are crucial material characteristics from the analytical point of view. Moisture content, which is a supply of water and steam, which is the single constituent that is driving most of the structural response. Permeability of the material, which is the resistance to flow and allows pore pressure to build up. Porosity of the material which gives us storage for expanding gases. Across ply tensile and shear strength which is associated with interlaminar failure. I-plane strain to failure which is necessary in the material to accommodate the incompressibility and associated with fiber direction failure (the pocketing event). The pore pressure potential, which is the driving force for most of the bad stresses, is influenced by the expansion measurement of the material and the constituent chemistry. In the area of wedge out, we have crack propagation in virgin material and in char material. Questions?

Thomas Greg, the theory sounds good, but in real life exit cones, we have had 3 firings in a row, TEM-7, TEM-8 and SM2, that did not have a ply angle change. Were they out of the normal range, or were they on the upper or lower limit?

Crose We don't have fully coupled analysis up and running. Maybe we can start to capture these subtleties analytically. If we can't refine our analysis to the point where we can do it that way, then we have to resort to a statistical game to know what is responsible for the changes. The primary benefit of this type of analysis is design. As you can see, I can change my design so as to stay away from those kind of problems, if I have design space to work within. If I don't have design space to work within, then we work harder on refining our analysis to make it more accurate and we have to adjust the material acceptance criteria or the controls for manufacturing processes, or perhaps, a combination of everything.

Upton Thank you, Greg. I have a couple of copies of the proceedings from our last meeting in November that I am going to leave up here for whoever would like a copy. Tomorrow morning, meet downstairs at 8:00 to leave from here to go to Michoud. Good night and thank you for coming.

APPENDIX A

TONY DAY

Laws Governing Environmental Compliance

Montreal Protocol

Signed by U. S. and 30 other nations in Sept 1987 after convincing evidence of CFC influence on the Ozone Layer.

Established timetable for production decrease of 50% in 10 years of 5 main CFC's.

In 1990, new evidence showed Ozone Layer depleting faster than previous data. This prompted a revised Montreal Protocol.

The Revision:

All CFC's, CCl₄, and Halons must cease production by 2000.

1,1,1-Trichloroethane should cease by 2002.

Action by President Bush on 11 February moves these dates up to 31 December 1995.

Clean Air Act of 1990

Became law 15 November 1990.

Contains directives for controlling toxic emissions.

Divides Ozone Depleting Substances into Classes

Class 1 - CFC's, halons, CCl₄, and 1,1,1-Trichloroethane

All Class 1 chemicals to be phased out by 2000.

1,1,1-Trichloroethane to be phased out by 2002.

Class 2 - HCFC's

HCFC's to be phased out by 2030.

Phase out Schedule as of 13 March 1992 was:

CFC's - 50% by 1995, but is now 50% by 1992

85% by 1997, but is now 100% by 1995

100% by 2000, now WITHDRAWN FROM COMMERCE IN 1996.

1,1,1-Trichloroethane - 30% by 1995, now 50% by 1992

70% by 2000, now 100% by 1995

HCFC's - Production Freeze by 2015
Phase-out Production by 2030
100% by 2002, now WITHDRAWN FROM COMMERCE IN 1996.

Enforcement -

Up to \$200K fines

Field Inspection/Citation Program.

Compliance Schedules of up to 12 months.

\$5000/day fines for violations.

Up to \$10,000 rewards for citizens who provide information leading to convictions or penalty.

Cost Increases -

Excise taxes are currently enforced on Ozone Depleting Substances.

Excise Tax= (base tax) x (ozone depleting potential) x (pounds used)

Base Taxes are:

1991 \$1.37	1994 \$2.65	1997 \$4.00
1992 \$1.67	1995 \$3.10	1998 \$4.45
1993 \$2.65	1996 \$3.10	1999 \$4.90
		2000 \$5.35

Cost of Freon 113 in 1987 was approx. \$600/bbl.

Cost of Freon 113 in 1991 was approx. \$2000/bbl.

Costs expected to escalate sharply with the President's 11 February announcement.

The demand for new cleaning equipment and alternative solvent systems may well outstrip supplier capacity.

Toxic Substance Control Act (TSCA)

CFR-40 (Code of Federal Regulations Title 40), Parts 700-789, July 1990, page 556. TSCA Subchapter R.

Denotes EPA materials for control per TSCA.

APPENDIX B

BOB BUNKER

**SOME IDEAS ON TESTING AND PROPERTIES OF NOZZLE
MATERIALS FOR USE IN THERMOSTRUCTURAL ANALYSES**

**ROBERT C. BUNKER
THIOKOL CORPORATION**

***Thiokol* CORPORATION**

Information on this page was prepared to support an oral presentation and cannot be considered complete without the oral discussion.

-
- IT HAS BEEN GENERALLY CONCEIVED BY MANY ENGINEERS THAT BOTH THERMAL AND MECHANICAL PROPERTIES ARE A FUNCTION OF THE THERMAL STATE (TEMPERATURE ONLY) AND MANY CODES ARE DESIGNED TO ACCEPT PROPERTIES AS A FUNCTION OF TEMPERATURE ONLY.
 - IN REALITY THE PROPERTIES ARE A FUNCTION OF SEVERAL STATES:
 - THERMAL STATE
 - CHEMICAL STATE
 - STRESS OR STRAIN STATE
 - MOISTURE CONTENT
 - POROSITY & PORE PRESSURE

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**THERMAL AND MECHANICAL PROPERTIES WHICH SHOULD BE
DETERMINED BASED UPON DIFFERENT STATES, THERMAL, CHEMICAL,
STRAIN, MOISTURE, ETC.**

- THERMAL CONDUCTIVITY
- SPECIFIC HEAT
- DENSITY
- PERMEABILITY
- POROSITY
- MODULUS
- POISONS RATIO
- COEFFICIENT OF THERMAL EXPANSION
- OTHERS

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and cannot be considered complete without the oral discussion.

HOW DO WE MODEL OR TRACK THE DIFFERENT STATES WHEN ANALYZING A NOZZLE COMPONENT

- TEMPERATURE STATE

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (K \nabla T) + C_{pg} \left(\frac{1}{\mu_g} \nabla P \right) \nabla T + \rho_g Q \frac{\partial \beta}{\partial T}$$

storage conduction convection generation

- CHEMICAL STATE

$$\frac{\partial B_i}{\partial t} = Ke^{-\frac{\Delta H}{RT}} (1B_i)^p$$

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- **MOISTURE STATE**

$$\frac{\partial M}{\partial t} = \nabla \cdot (D \nabla M) + \frac{\partial M_i}{\partial t}$$

- **PORE PRESSURE**

$$\phi \eta \frac{\partial P}{\partial t} = \underbrace{\frac{\eta}{\mu_g} \nabla \cdot (P T \nabla P)}_{\text{storage}} + \underbrace{\frac{1}{T} \left(\frac{\eta}{\mu_g} P T \nabla P \right) \nabla T + \frac{\phi \eta}{T} \left(\frac{\partial T}{\partial t} \right) P + \rho_u \frac{\partial \beta}{\partial t}}_{\text{convection generation}}$$

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**EXAMPLES OF WHY WE KNOW THE PROPERTIES ARE FUNCTIONS OF THE STATE AND
DIFFERENT FROM TEMPERATURE**

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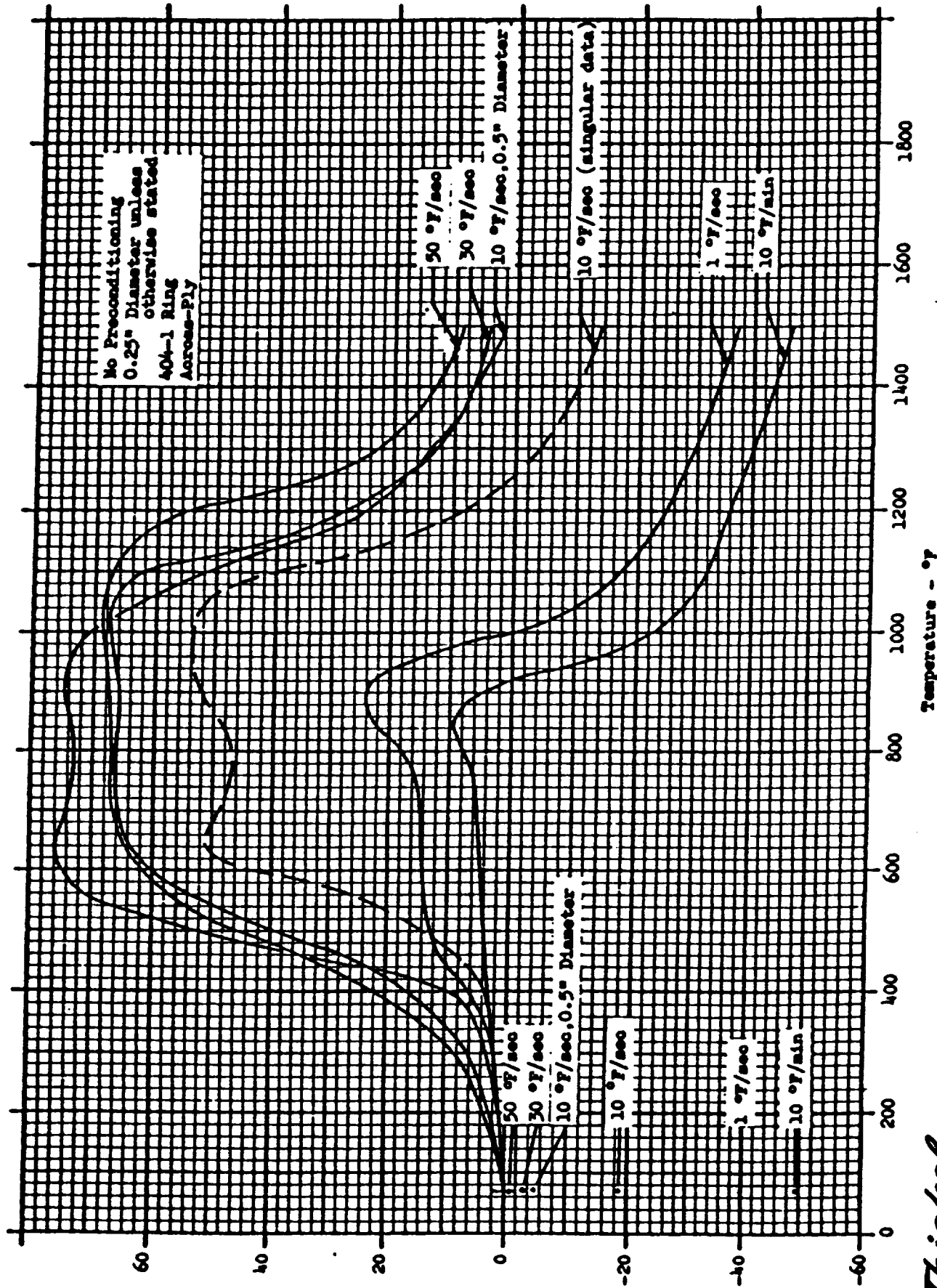
Information on this page was prepared to support an oral presentation
and cannot be considered complete without the oral discussion.

RECOMMENDATIONS

- FUTURE CODES SHOULD BE DEVELOPED TO ACCEPT PROPERTIES AS A FUNCTION OF SEVERAL STATES.
- FUTURE CODES SHOULD BE DEVELOPED TO COMPUTE OTHER STATES BASED UPON THE THERMAL CHEMICAL, MOISTURE AND MECHANICAL LOADING HISTORY
- MATERIAL TEST PLANS SHOULD BE DESIGNED TO OBTAIN THE PROPERTIES AS A FUNCTION OF THE DIFFERENT STATES.
- MODEL ALL OF LABORATORY TESTS USING THE COMPUTER MODEL TO BETTER INTERPRET TEST RESULTS AND ASSESS THE EFFECTS OF THOSE PARAMETERS THAT ARE LEAST KNOWN EG. EVALUATE THE RESULTS OF STRESS/STRAIN DATA BASED UPON CHEMICAL STATE.
- WE SHOULD MAKE AN ATTEMPT TO MEASURE SOME OF THE STATE PROPERTIES IN SITU FOR BOTH MECHANICAL AND THERMAL PROPERTIES.
- MEASURE ELECTRICAL CONDUCTIVITY DURING STRESS/STRAIN TESTS TO EVALUATE CHEMICAL STATE DURING TEST.
- RELATE ELECTRICAL CONDUCTIVITY TO STATE BY MEASURING CONDUCTIVITY IN TGA AND/OR DCS TESTS.
- EVALUATE THERMAL AND ELECTRICAL CONDUCTIVITY IN THERMAL CONDUCTIVITY TESTING AT DIFFERENT STRESS STRAIN LEVELS.

Thiokol CORPORATION

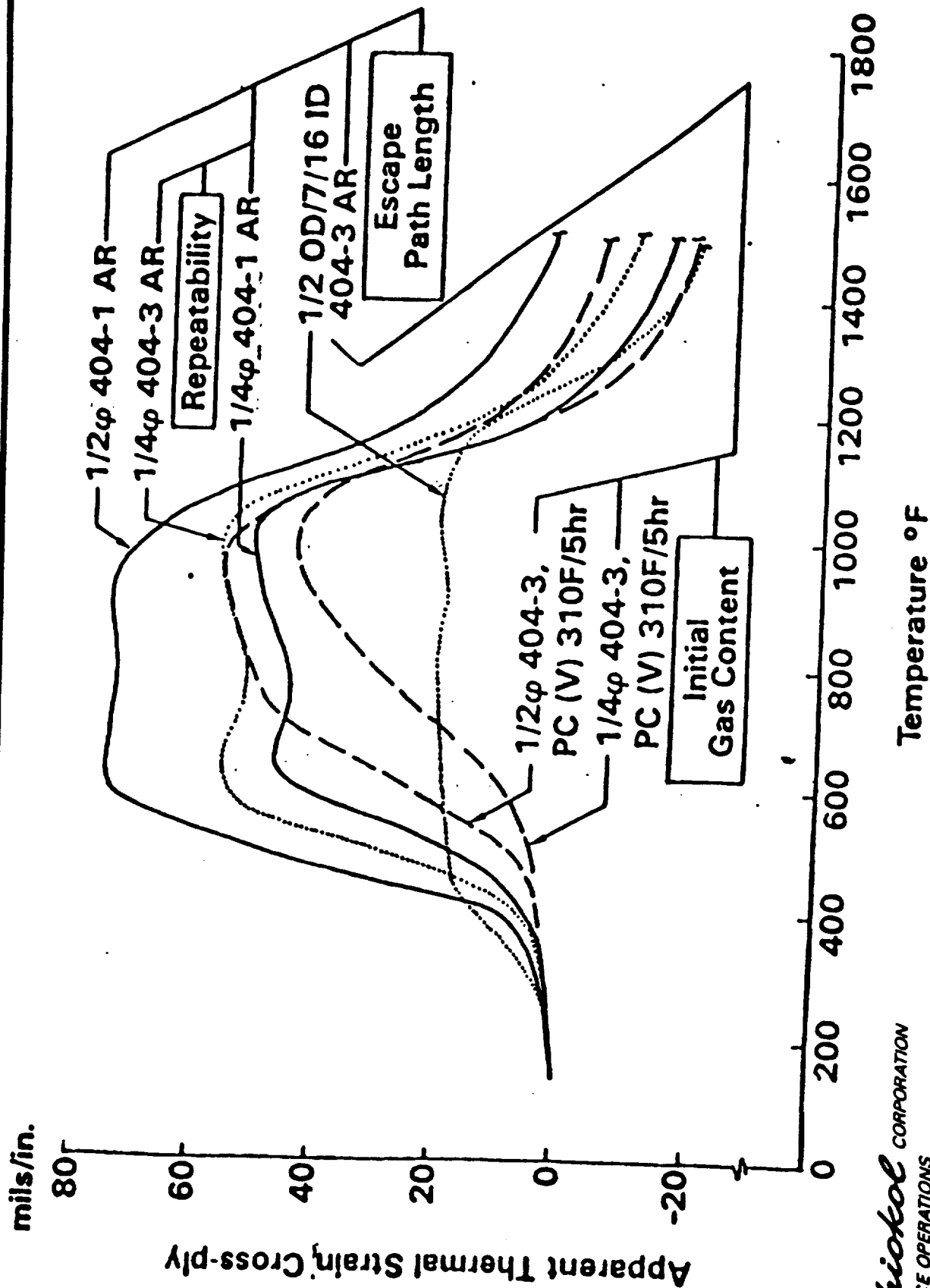
Information on this page was prepared to support an oral presentation and cannot be considered complete without the oral discussion.



Thiokol CORPORATION
SPACE OPERATIONS

INFORMATION ON THIS PAGE WAS PREPARED TO SUPPORT AN ORAL PRESENTATION
AND CANNOT BE CONSIDERED COMPLETE WITHOUT THE ORAL DISCUSSION

ACROSS PLY EXPANSION FOR VARIOUS DIAMETER CTE SPECIMENS AT 10° F/SEC HEATING RATE



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SPACE OPERATIONS

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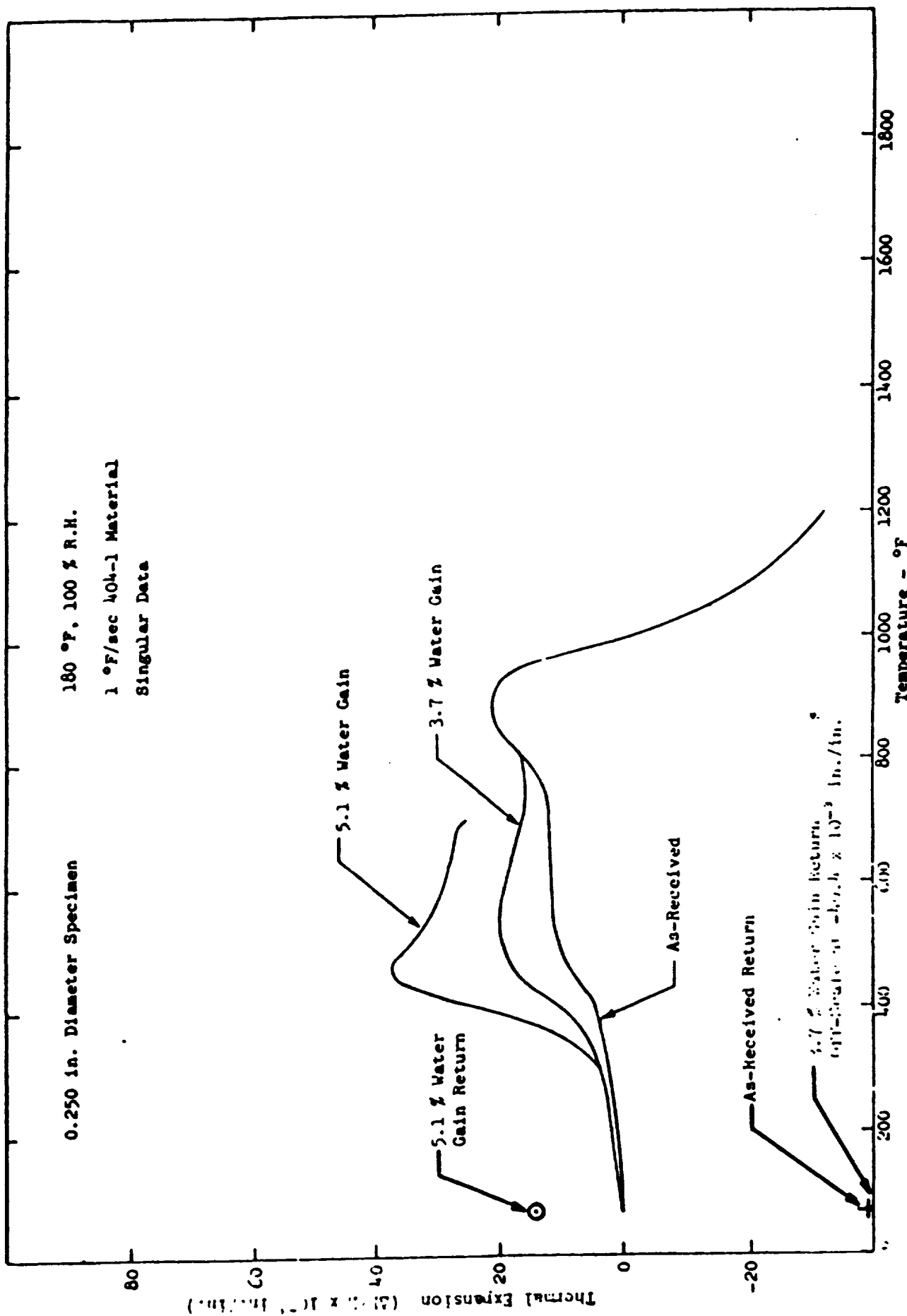
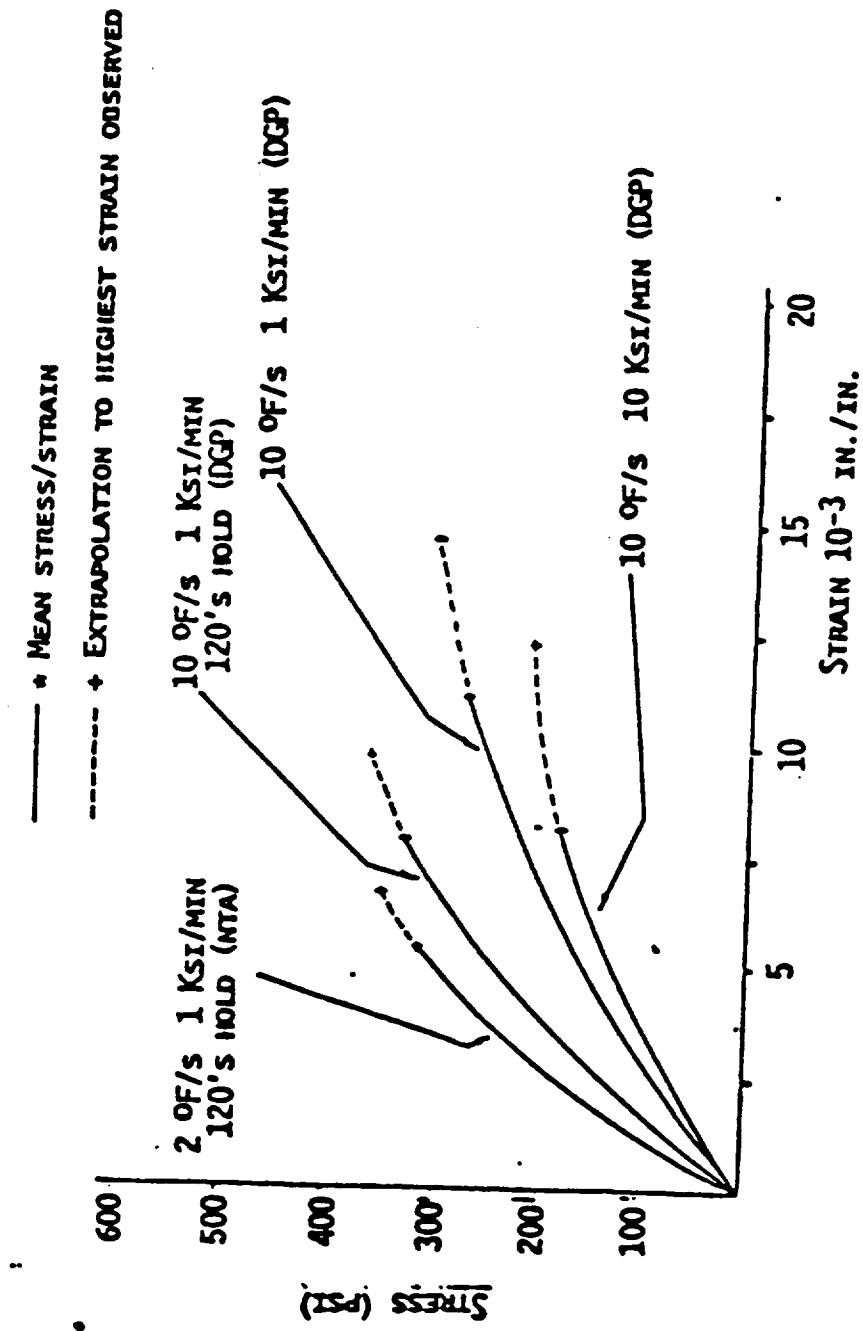


Figure 3.15.2-5. Across-Ply Thermal Expansion of Humidified PM 5055 Carbon Phenolic

Thiokol CORPORATION
SPACE OPERATIONS

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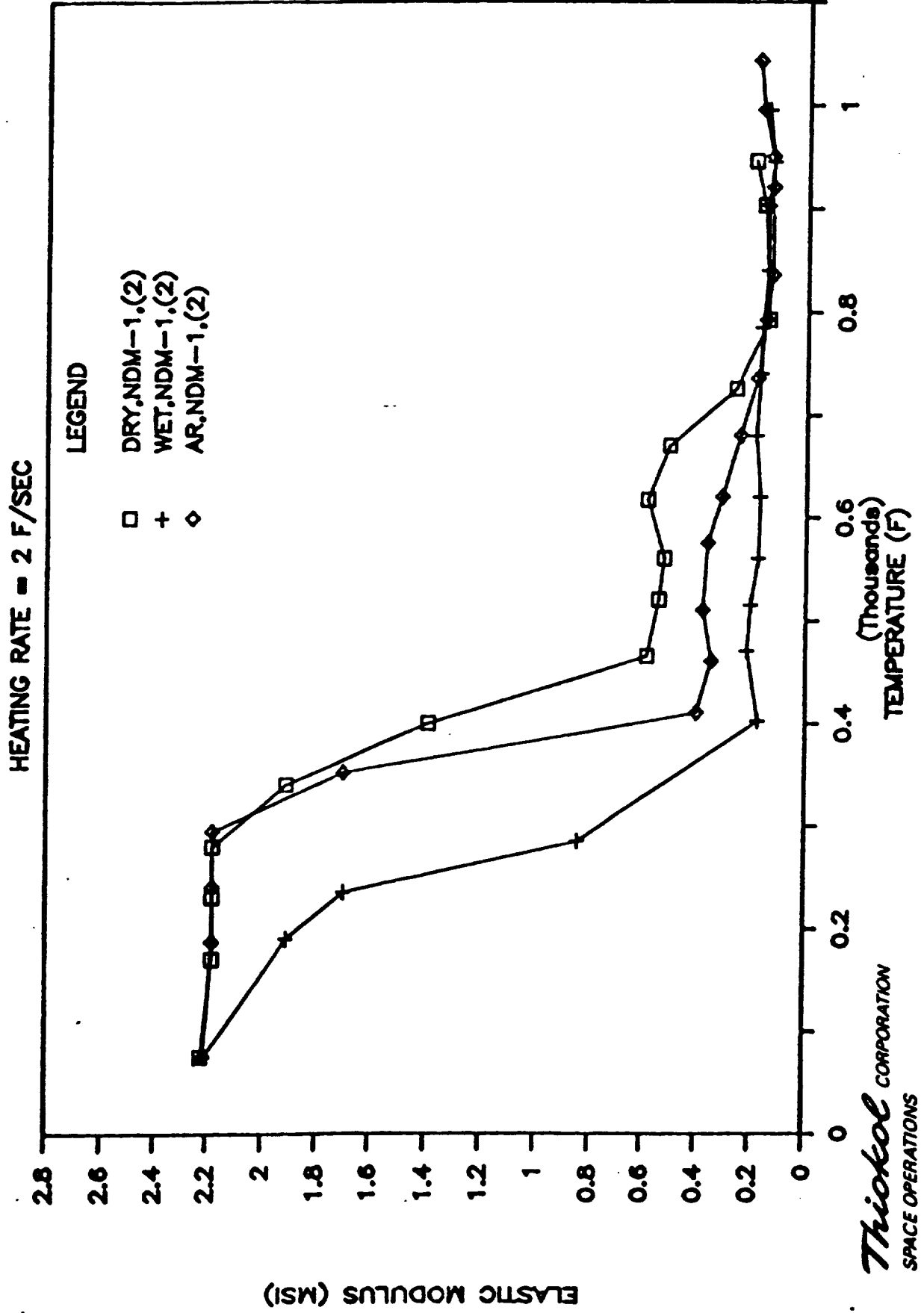
Probable Value Curves for FM5055 Across-Ply Tension under Various Conditions at 750 °F



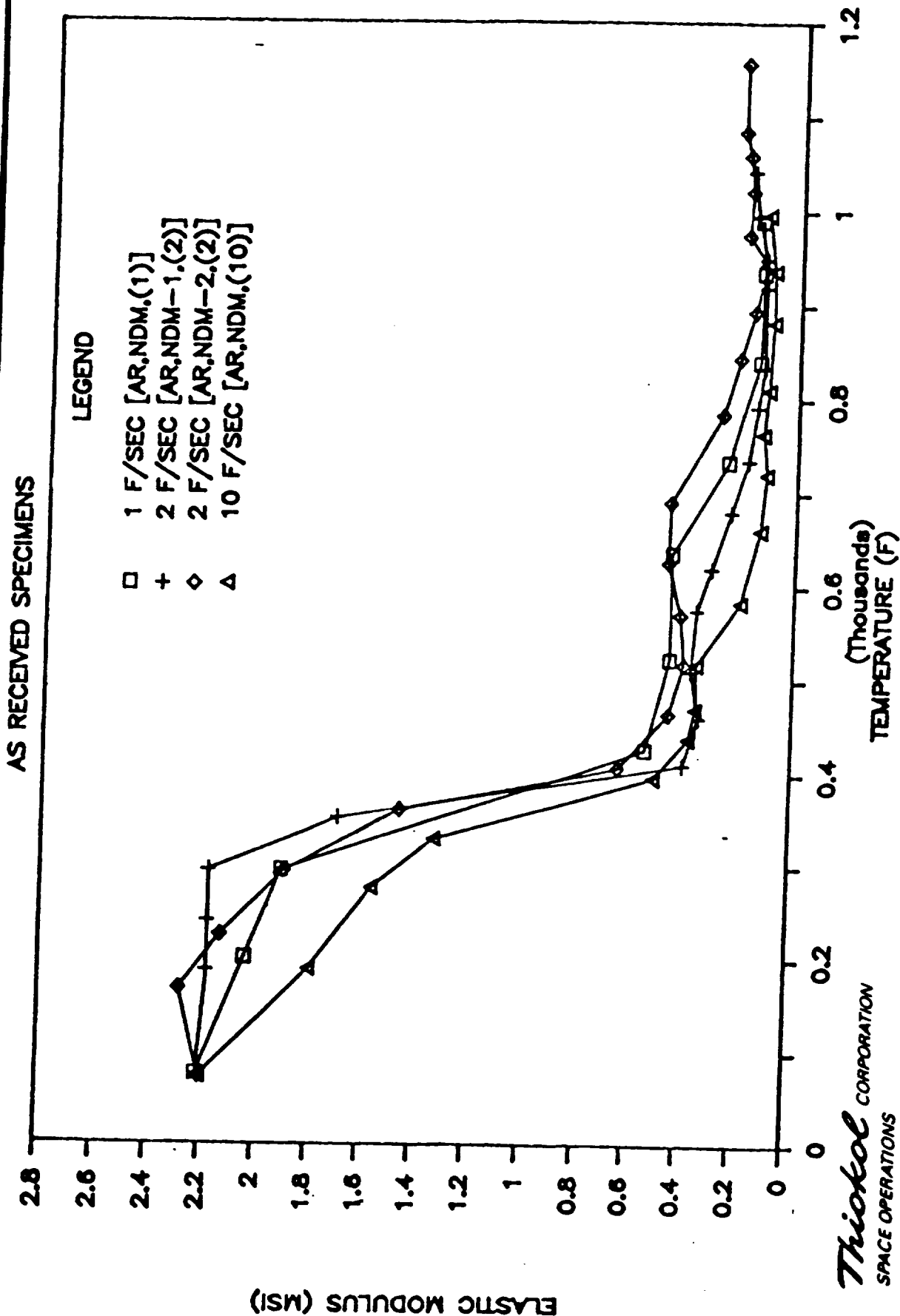
Thiokol CORPORATION
SPACE OPERATIONS

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NONDESTRUCTIVE ELASTIC MODULUS



NONDESTRUCTIVE ELASTIC MODULUS



APPENDIX C

ERIC STOKES

SELECTION OF ACCEPTANCE TESTS FOR CURED

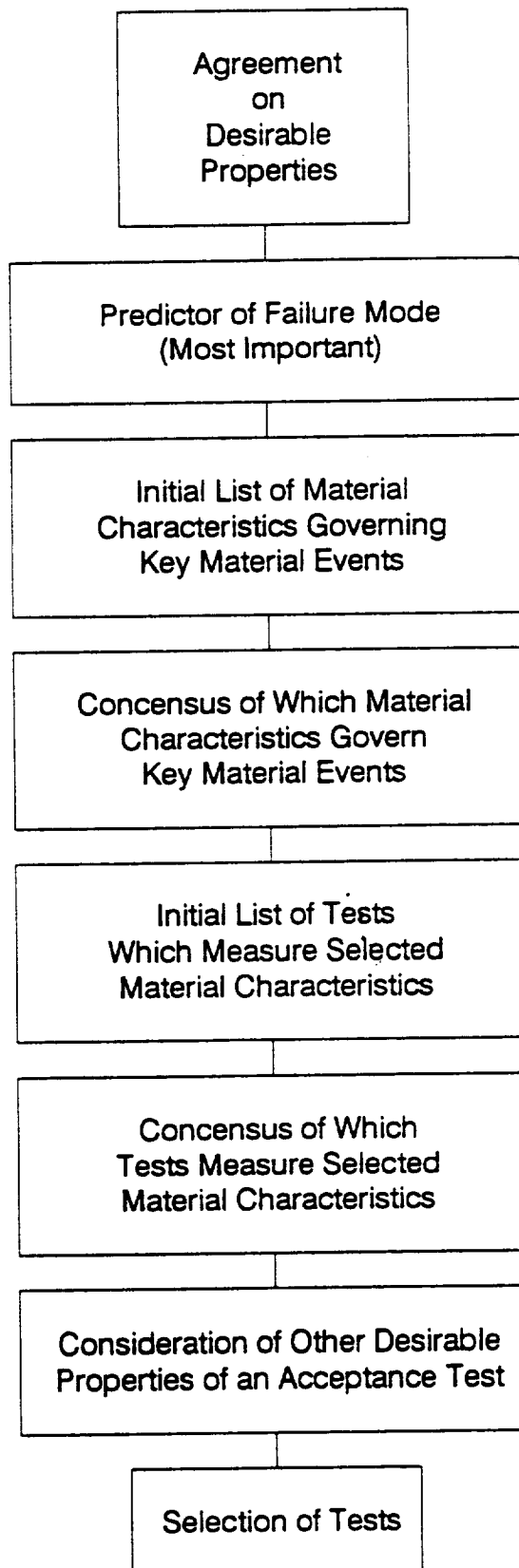
CARBON PHENOLICS

**E.H. Stokes
Southern Research Institute
Birmingham, Alabama**

Presented At

**Solid Propulsion Integrity Program Industry Advisory Committee Meeting
New Orleans, Louisiana
May 14 - 15, 1992**

PROCESS FOR SELECTION OF
NEW / IMPROVED ACCEPTANCE TESTS

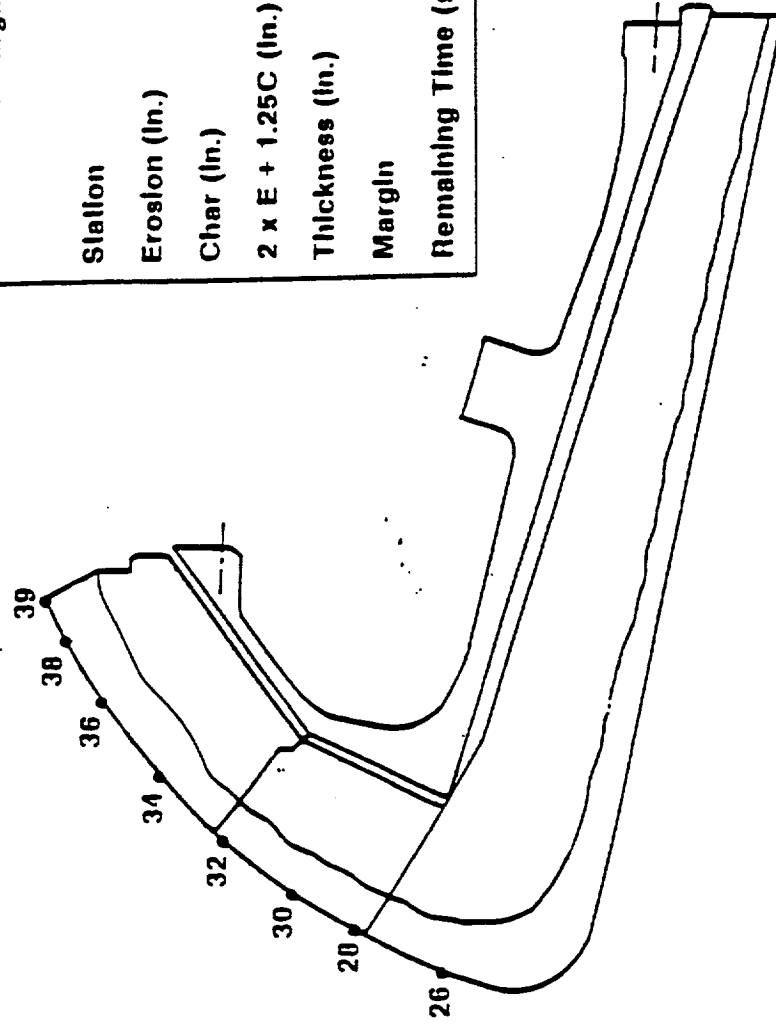


DESIRABLE PROPERTIES OF AN ACCEPTANCE TEST

1. Predictor of Failure Mode
2. Measures Other Desirable Properties
3. Sensitive
4. Accurate
5. Precise
6. Timely
7. Minimal Cost
8. Simple
9. Material Property

EROSION RATE

Minimum Margins of Safety	
Station	Alt Ring 34 (345 deg)
Erosion (ln.)	1.39
Char (ln.)	0.41
2 x E + 1.25C (ln.)	3.29
Thickness (ln.)	3.24
Margin	-0.02
Remaining Time (sec)	162



EROSION RATE

Possible Results

- Lower Margins of Safety
- Changes in Throat Dimensions (Thrust)

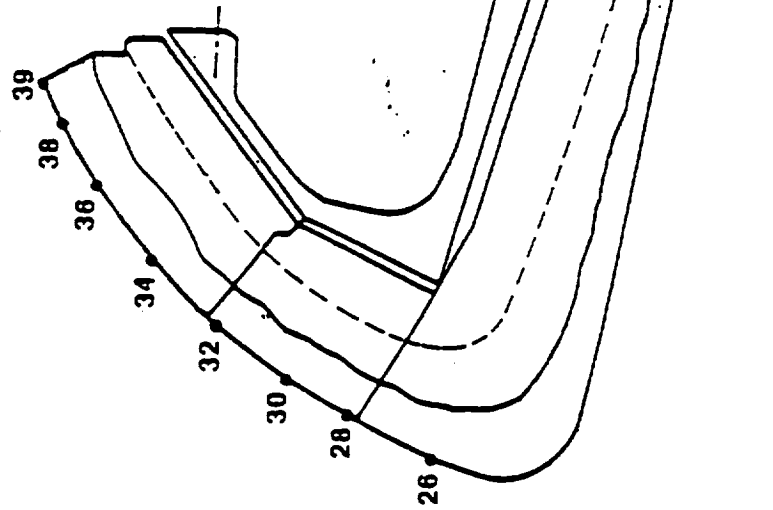
Properties That Result in Higher Susceptibility to Event

- o Lower Yam Carbonization Temperatures Result in Less Graphitic Structure in Yam
- o Higher Resin Contents

Examples

- o Many

CHAR DEPTH



Minimum Margins of Safety	
Station	All Ring 34 (345 deg)
Erosion (in.)	1.39
Char (in.)	0.41
2 x E + 1.25C (in.)	3.29
Thickness (in.)	3.24
Margin	-0.02
Remaining Time (sec)	162

CHAR DEPTH (BACKFACE TEMPERATURE)

Possible Results

- Lower Margins of Safety
- Destruction of Adhesive on Backface of Carbon
- Backface Gas Pressures

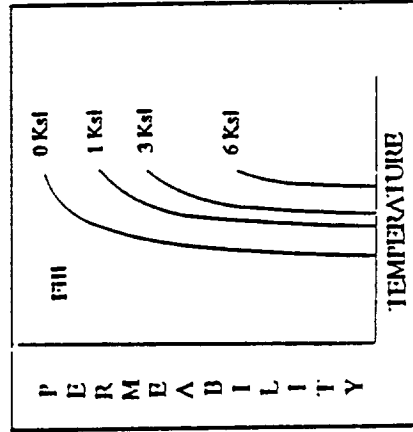
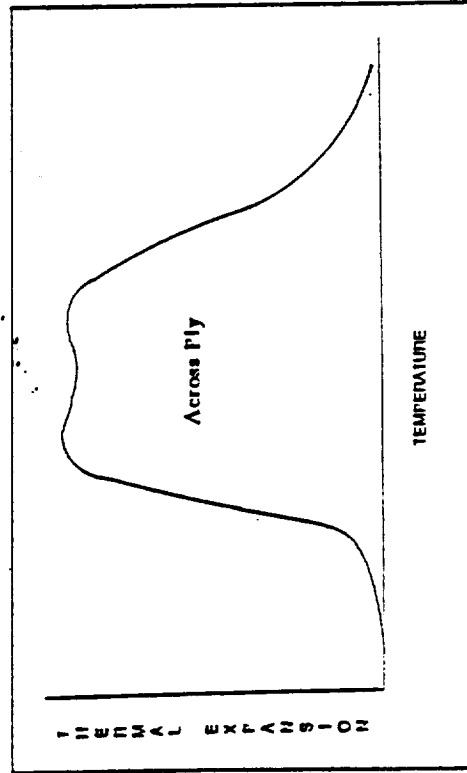
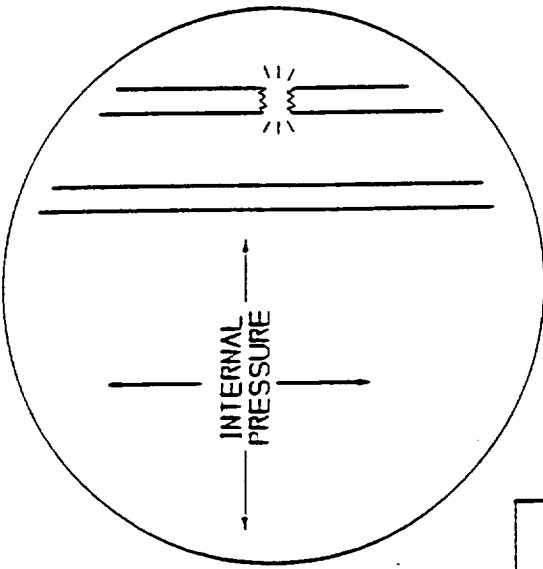
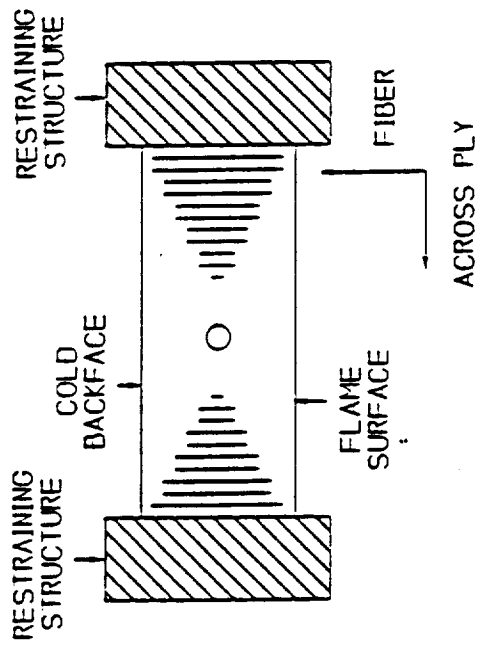
Properties That Result in Higher Susceptibility to Event

- o Higher Thermal Conductivities
- o Lower Heats of Pyrolysis

Examples

- o Many

POCKETING



POCKETING

Possible Results

- Burn Through
- Higher Erosion Rates
- Disruption of Flow Field

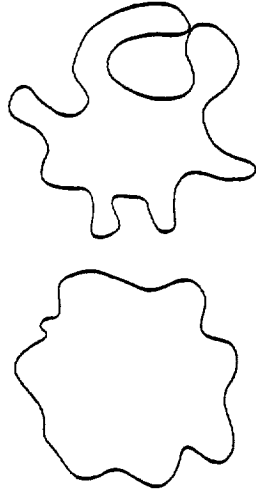
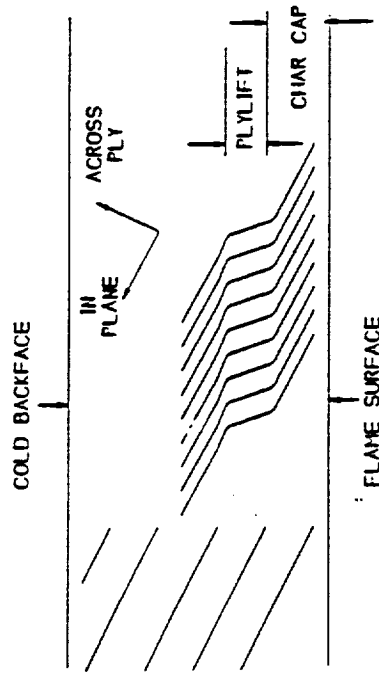
Properties That Result in Higher Susceptibility to Event

- o Lower Yarn Strengths
- o Lower Elevated Temperature In-Plane Permeability As a function of Across Ply Compressive Stress
- o Higher Across Ply Thermal Expansion
- o Lower Char Yield (Higher Moles of Gas Produced)

Examples

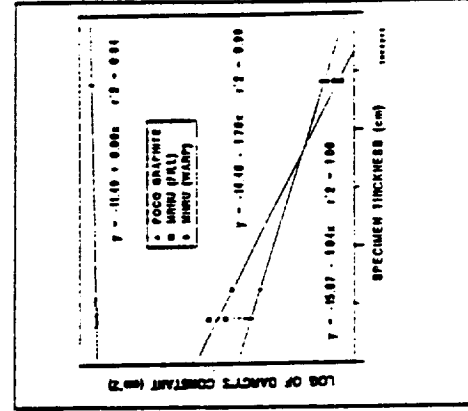
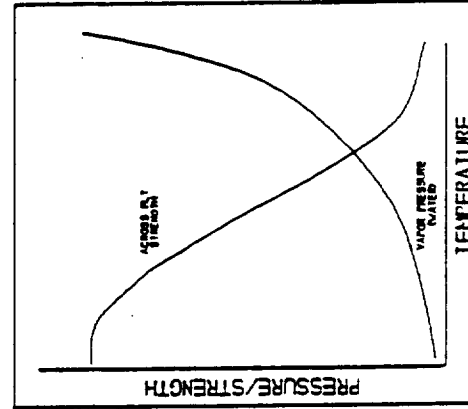
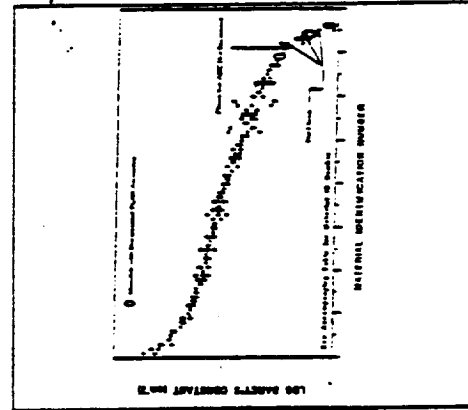
- 8A FWD Nose Ring
- 8A AFT Inlet Ring

PLYLIFT



LOW PERMEABILITY

HIGH PERMEABILITY



PLYLIFT ***(CHAR CAP REMOVAL)***

Possible Results

- Burn Through
- Higher Erosion Rates
- Disruption of Flow Field

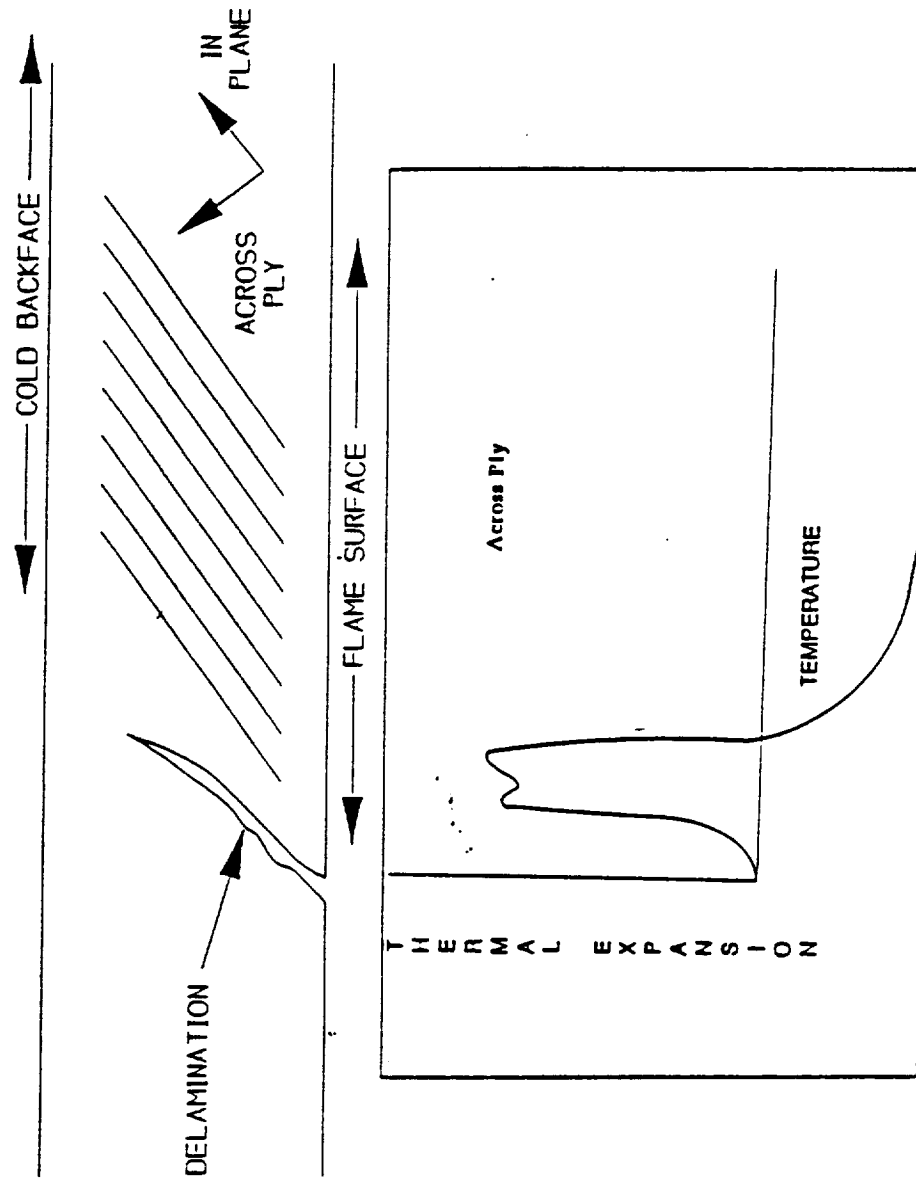
Properties That Result in Higher Susceptibility to Event

- o Low Temperature Permeability
- o Lower Across Ply Tensile Strength (Minor Role)
- o Higher Volatiles Content (Only Under Some Conditions)
- o Low Moisture Content
- o 500°F Strain-To-Failure

Examples

- ETM-1A AEC
- FSM-1 AEC
- TEM-6 AEC
- 15B COWL

DELAMINATIONS



DELAMINATIONS

Possible Results

- Lower Margins of Safety
- Greater Char Depth

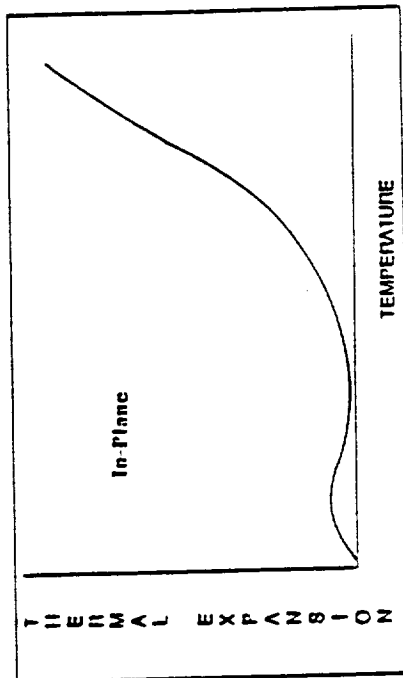
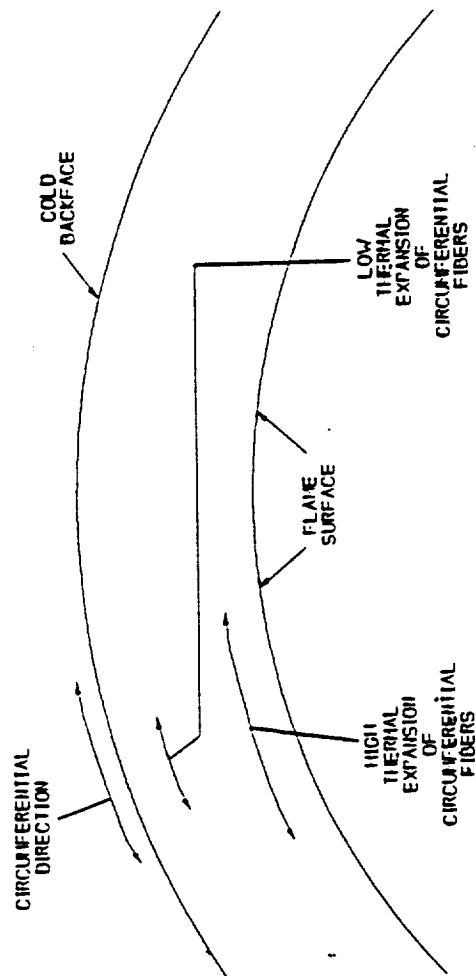
Properties That Result in Higher Susceptibility to Event

- o Higher Across Ply Contraction
- o Lower Across Ply Tensile Strength
- o Lower Char Yield

Examples

- Many

THERMOSTRUCTURAL FAILURE



RESULT: Circumferential Fibers at Low Temperature In Tension. If Tensile Forces Exceed Strength of Fibers, Fibers Fail.

THERMOSTRUCTURAL

Possible Results

- Yarn Breakage
- Reduced Structural Integrity

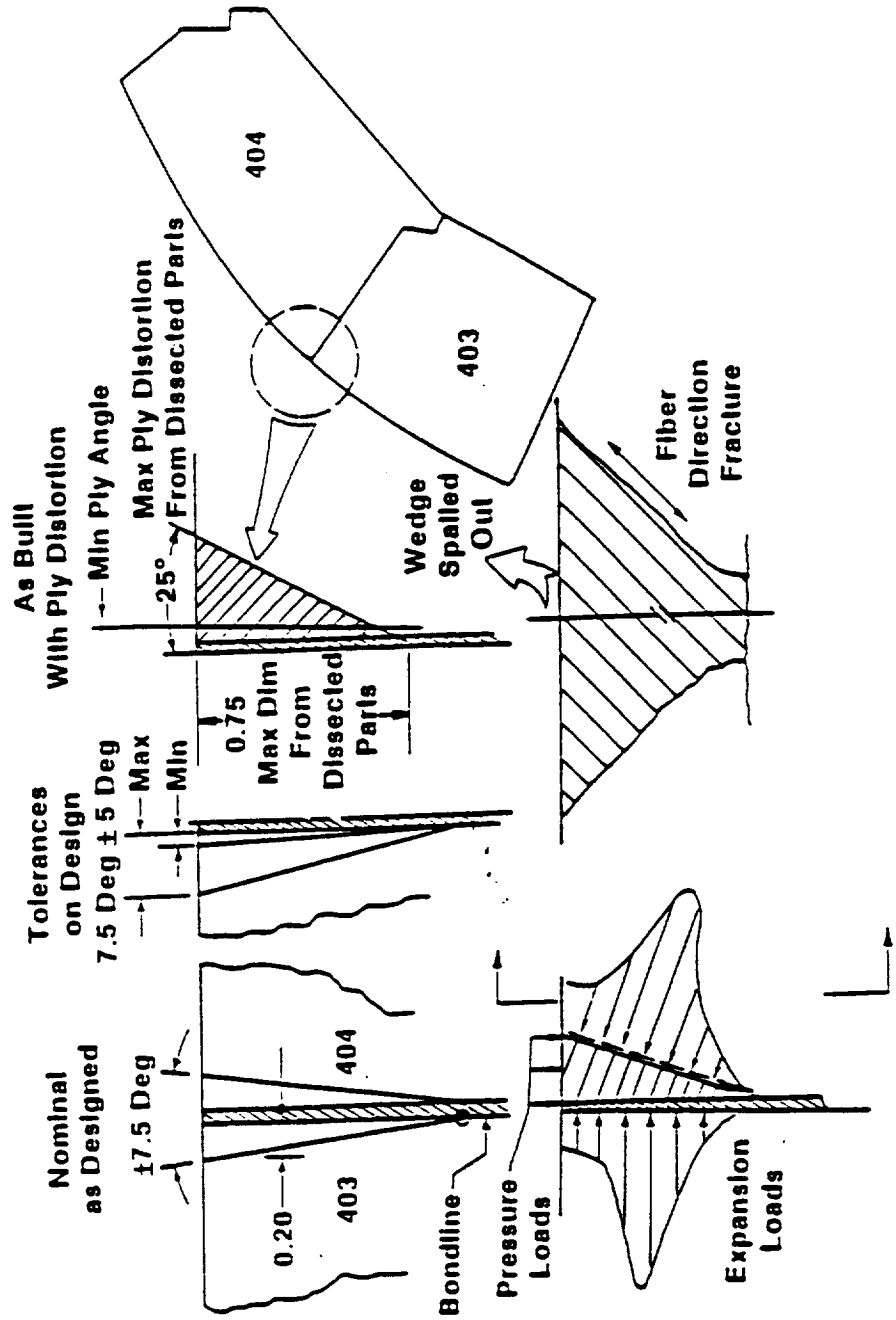
Properties That Result in Higher Susceptibility to Event

- o High Yarn Thermal Expansion
- o Low Yarn Strength
- o High Yarn Modulus

Examples

- o None With Carbon Phenolic
- o Some With Carbon-Carbons

WEDGEOUT



WEDGEOUT

Possible Results

- Lower Margins of Safety
- Greater Char Depth

Properties That Result in Higher Susceptibility to Event

- o Higher Across Ply Thermal Expansion
- o Lower Permeability
- o Lower Interlaminar Shear Strength

Examples

- 10B FWD Nose Ring
- 10B AFT Inlet Ring

Material Properties Governing Key Material Events

<u>EVENT</u>	<u>PRIMARY FACTORS</u>	<u>SECONDARY FACTORS</u>
Erosion Rate	Yarn Carbonization Temperature Resin Content	Char Yield Filler Content
Char Depth (Back Face Temperature)	Thermal Conductivity	Heat of Ablation
Pocketing	Yarn Strength, ET Permeability f(AP Comp. Stress)	Char Yield (Moles of Gas Produced) Across Ply Thermal Expansion
Plylift	Low Temperature Permeability 500°F Strain-To-Failure	Across Ply Tensile Strength Moisture Content Volatile Content
Delamination	Across Ply Contraction	Across Ply Tensile Strength/Modulus Char Yield
Thermostructural	In-Plane Strength/Modulus In-Plane Thermal Expansion	
Wedgeout	Across Ply Thermal Expansion Permeability	Char Yield (Moles of Gas Produced) Interlaminar Shear Strength

NAME _____

SURVEY 1

LIST THOSE PROPERTIES OF AN ACCEPTANCE TEST THAT ARE DESIRABLE

	<u>Desirable</u>	<u>Not Desirable</u>	<u>Not Sure</u>
Predictor of Failure Mode	_____	_____	_____
Measures Other Desirable Properties	_____	_____	_____
Sensitive	_____	_____	_____
Accurate	_____	_____	_____
Precise	_____	_____	_____
Timely	_____	_____	_____
Minimal Cost	_____	_____	_____
Simple to Perform	_____	_____	_____
Material Property	_____	_____	_____

LIST OTHER PROPERTIES OF AN ACCEPTANCE TEST THAT MAY BE DESIRABLE

NAME _____

SURVEY 2

**RANK RELATIVE IMPORTANCE OF PROPERTY OF AN ACCEPTANCE TEST
FOR CURED CARBON PHENOLIC COMPOSITES**

	<u>Rank</u>
Predictor of Failure Mode	_____
Measures Other Desirable Properties	_____
Sensitive	_____
Accurate	_____
Precise	_____
Timely	_____
Minimal Cost	_____
Simple to Perform	_____
Material Property	_____
Additional Property A	_____
Additional Property B	_____
Additional Property C	_____
Additional Property D	_____
Additional Property E	_____

NAME _____

SURVEY 3

LIST TO THE BEST OF YOUR ABILITY THOSE MATERIAL PROPERTIES OF
CURED CARBON PHENOLIC COMPOSITES THAT ARE GOVERNING
THE FOLLOWING KEY MATERIAL EVENTS

<u>EVENT</u>	<u>PRIMARY FACTORS</u>	<u>SECONDARY FACTORS</u>
Erosion Rate	<hr/> <hr/> <hr/>	<hr/> <hr/> <hr/>
Char Depth (Back Face Temperature)	<hr/> <hr/> <hr/>	<hr/> <hr/> <hr/>
Pocketing	<hr/> <hr/> <hr/>	<hr/> <hr/> <hr/>
Plylift	<hr/> <hr/> <hr/>	<hr/> <hr/> <hr/>
Delamination	<hr/> <hr/> <hr/>	<hr/> <hr/> <hr/>
Thermostructural	<hr/> <hr/> <hr/>	<hr/> <hr/> <hr/>
Wedgeout	<hr/> <hr/> <hr/>	<hr/> <hr/> <hr/>

APPENDIX D

CURT LOOMIS

M/VISION Materials Software System

- Materials Software System started in 1982 as IR&D Program
- Initial Prototype tested by 16 companies
- First commercial M/VISION system delivered in August, 1990
- Over 30 sites installed



STME Materials Database

Objective: Develop a valid and comprehensive common materials database to support the STME development. The database will be electronic and will contain materials property data that directly supports the STME design.

Approach: Utilize a government and contractor concurrent engineering team to insure that the STME materials database meets the "user" needs.

Team "Process" Highlights:

- 1st Quality Function Deployment(QFD) prioritized technical requirements
- Evaluated existing database architecture
- Drafted Approval Agency charter
- 2nd QFD established preliminary guidelines for materials data

STME Materials Database(cont.)

Team "Process" Highlights(cont.):

- Approval Agency formed with government and contractor representatives
- Provided focus to the hydrogen standardization round robin test program to insure that critical test parameters/lab to lab variations are assessed and understood
- Approval Agency developed standard reporting data formats for pertinent mechanical properties
- Working groups gathered pedigreed materials data packages to assess accept/reject criteria for pertinent mechanical properties
- Selected M/Vision as the common materials database software system
- Developed guidelines for time-phased materials characterization testing (guidelines to be used by Component Development Teams in developing their specific materials test plans)

STME Materials Database(cont.)

Materials Database Uses:

- Proper documentation of the material's pedigree will insure that the data collected is fully characterized and is acceptable to the government/contractor team. This will help remove data controversies from analyses issues.
- Existence of actual data(raw data) allows all members of the design team to use the data for conventional analyses as well as specialized analyses. The easy access to materials property data allows reliability and sensitivity studies to be performed easily and with more meaning.
- Simplifies data reduction and provides traceability of the methods used for data manipulation.
- Provides a simple means to export linear and non-linear materials data in IGES, PATRAN Neutral File, spreadsheet, or user-defined formats to analysis codes.

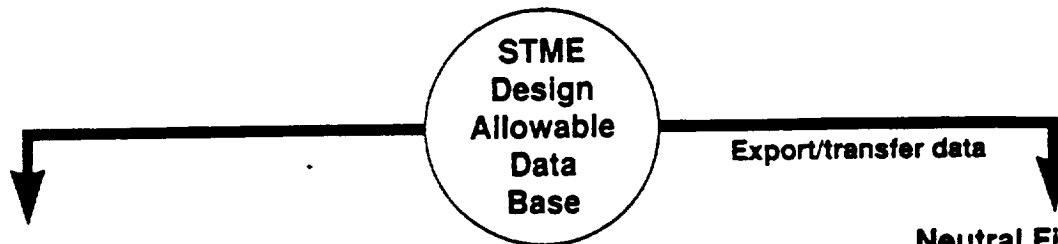
STME Materials Database(cont.)

Materials Database Uses(cont.):

- Facilitates data exchange between the contractors and MSFC
- Facilitates sharing of common materials data and eliminates materials test duplication
- Streamlines materials data flow(one electronic data file required from the originating test lab to the database). Database contains the raw materials data and the design allowable curves in one place
- Allows for the easy identification of materials/properties lacking adequate characterization

STME Design Allowable Data Base

Provides Foundation for Design and Analysis



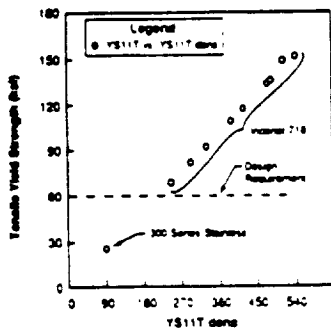
Evaluate Material Properties for Design

Key design criteria and properties

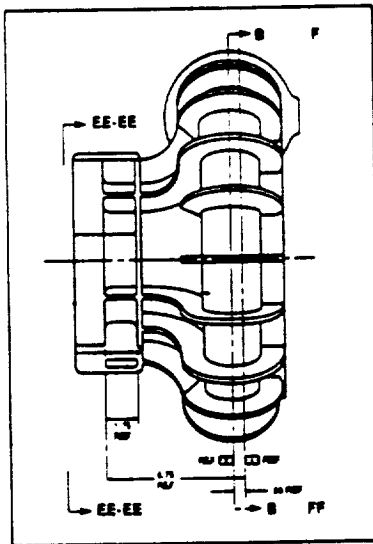
- Tensile strength > 125 ksi
- LCF life > 10^4 cycles
- Lox compatible



Material Selection



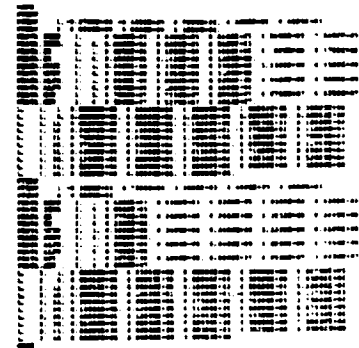
Detailed Design Process



Final Component Design



Neutral File (today) CALS/PDES (future)

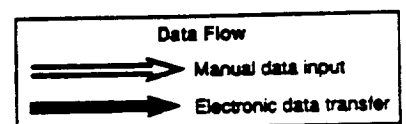


Neutral file

Import data
to model



Finite Element Analysis Model



STANDARD DATA FORMAT FOR COMPUTERIZATION OF
TENSILE TEST DATA (ASTM TEST METHOD E 8, 21, 338, 602)

CONDITIONALLY ACCEPTABLE DATA

FIELD <u>No. #</u>	FIELD <u>NAME AND DESCRIPTION</u>	CATEGORY SETS VALUES <u>OR UNITS, SI (US CUST)</u>
-----------------------	--------------------------------------	---

MATERIAL IDENTIFICATION

1.	Measurement units	Alpha-numeric string
2.	UNS number	Alpha-numeric string
3.	Commercial name	Alpha-numeric string
4.	Material Identification	Alpha-numeric string

SPECIMEN INFORMATION

5.	Specification number	Alpha-numeric string
6.	Material form	Alpha-numeric string
7.	Heat treat condition, beginning (Table P4)	Alpha-numeric string
8.	Heat treat condition, final (Table P4)	Alpha-numeric string
9.	Heat number	Alpha-numeric string
10.	Heat treat ID number	Alpha-numeric string
11.	Lot identification	Alpha-numeric string
12.	Mill ID number	Alpha-numeric string
13.	Forging serial number	Alpha-numeric string
14.	Grade (cast material)	Alpha-numeric string
15.	Grain size (ASTM)	Numeric
16.	Phases	Alpha-numeric string
17.	Dispersions	Alpha-numeric string
18.	Pre-fabrication dimensions	Alpha-numeric string
19.	Special specimen fabrication process (Table P5)	Alpha-numeric string
20.	Specimen type (Code only) (Table T1)	Alpha-numeric string
	RECTANGULAR TENSION TEST SPECIMEN	CODE FTTS
	PIN-LOADED TENSION TEST SPECIMEN	CODE PLTS
	ROUND TENSION TEST SPECIMENS	
	STANDARD ROUND WITH THREADED ENDS	CODE RTHE
	STANDARD ROUND WITH THREADED ENDS AND SHOULDER	CODE RTES
	STANDARD ROUND WITH BUTTON HEAD ENDS	CODE RBHE
	STANDARD ROUND WITH BUTTON HEAD ENDS AND SHOULDER	CODE RBHS
	STANDARD ROUND WITH SHOULDER FOR HYDRAULIC GRIPS	CODE RSHG
	STANDARD FLAT NOTCH SPECIMEN	CODE FNOS
	NOTCHED, ROUND(AFTER E292)	CODE NORD
21.	Nominal K _t	Numeric
22.	Specimen orientation (Table P2)	Alpha-numeric string
23.	Specimen location (Table P3)	Alpha-numeric string
24.	Specimen gage diameter or thickness	mm (in)
25.	Specimen width (except cylindrical)	mm (in)
26.	Specimen cross-sectional area	mm ² (in ²)
27.	Test gage length	mm (in)
28.	Tensile UTS ,@ RT	MPa (ksi)
29.	YS 0.2% ,@ RT	MPa (ksi)
30.	%el ,@ RT	%
31.	%RA ,@ RT	%
32.	Modulus ,@ RT	GPa (msi)
33.	Density	kg/m ³ (lb/in ³)

HCF DATA									
EEL INFORMATION									
Requesting Engineer:			EEL Log No: 2-91-102		Charge #:		EWR:		
Test Engineer:			Date Rec'd:		Approved by:				
Test System:			Remarks:						
CONDITIONALLY ACCEPTABLE METADATA									
Material I D: INCO 903			Specification: 170-186		UNS NO:		Heat #: SCHLOSSER HH4183uk		
Special Test Considerations: NONE			Specimen Type: FHP-250		Specimen Orientation: LL				
Test Gage Length: 0.125			Grain Size:		Final Heat Treat Cond: STA-2		Density: 0.293		
Material Form: FORGING			Test Temp: AMB		Environment: AIR		Pressure(psi): AMB		
Chem Comp of Environment:					Specimen Fab Process: MAC		Test date: Apr-91		
Comments: MACHINING DOCUMENT 738037									
Control Mode: LOAD									
Wave Form: SINE									
R Ratio: -1									
Specimen ID	Gas Type	Temp F	Dia Orig	Freq HZ	R Ratio	Max Load (kips)	Max Stress (ksi)	Cycles to Failure	Failure Origin
1	AIR	AMB	0.2470	30	-1	2.6340	55.0	245606	CEH
2	AIR	AMB	0.2510	30	-1	2.1030	42.5	1291313	CEH
H-75	AIR	AMB	0.2480	30	-1	1.8110	37.5	8708500	DNF
91	AIR	AMB	0.2490	30	-1	3.6520	75.0	88080	CEH

PROPERTY

71.	Specimen Identification	Alpha-numeric string
72.	Specimen dimensions	Table T1
73.	Special test considerations (Table P1)	Table P1
74.	Yield strength method (Table T2)	Alpha-numeric string
75.	Yield strength offset or extension	mm (in)
76.	Yield strength load	N (lbf)
77.	Yield strength	MPa (ksi)
78.	Yield point method (Table T3)	Alpha-numeric string
79.	Yield point extension	mm (in)
80.	Yield point load	N (lbf)
81.	Maximum load	N (lbf)
82.	Ultimate tensile strength.	MPa (ksi)
83.	K_t (Will be footnote)	Numeric
84.	Gage length at fracture	mm (in)
85.	Total elongation	%
86.	Minimum area after fracture	mm ² (in ²)
87.	Reduction of area	%
88.	Modulus from tensile data	GPa (msi)
89.	Location of fracture in gage length (Table T4)	Alpha-numeric string
90.	K, strength coefficient	Numeric
91.	n, strain hardening exponent	Numeric
92.	True fracture strength	MPa (ksi)
93.	True fracture ductility	Numeric
94.	Bridgeman fracture strength	MPa (ksi)
95.	Is test valid per ASTM E8, E8M, E21?	Alpha-numeric string
96.	Comments	Alpha-numeric string
	Is fracture location in middle half of gage length?	Alpha-numeric string
	Figure:	
97.	Stress & strain @ P.L., 0% offset	MPa,% (ksi,%)
98.	Stress & strain @ 0.025% offset	MPa,% (ksi,%)
99.	Stress & strain @ 0.10% offset	MPa,% (ksi,%)
100.	Stress & strain @ 0.15% offset	MPa,% (ksi,%)
101.	Stress & strain @ yield strength	MPa,% (ksi,%)
102.	Stress & strain @ 0.20% offset	MPa,% (ksi,%)
103.	Stress & strain @ 0.50% offset	MPa,% (ksi,%)
104.	Stress & strain @ 1.0% offset	MPa,% (ksi,%)
105.	Stress & strain @ 1.5% offset	MPa,% (ksi,%)
106.	Stress & strain @ 2.0% offset	MPa,% (ksi,%)
107.	Stress & strain @ 2.5% offset	MPa,% (ksi,%)
108.	Stress & strain @ 3.0% offset	MPa,% (ksi,%)
109.	Stress & strain @ ultimate load	MPa,% (ksi,%)
110.	Stress & strain @ failure	MPa,% (ksi,%)

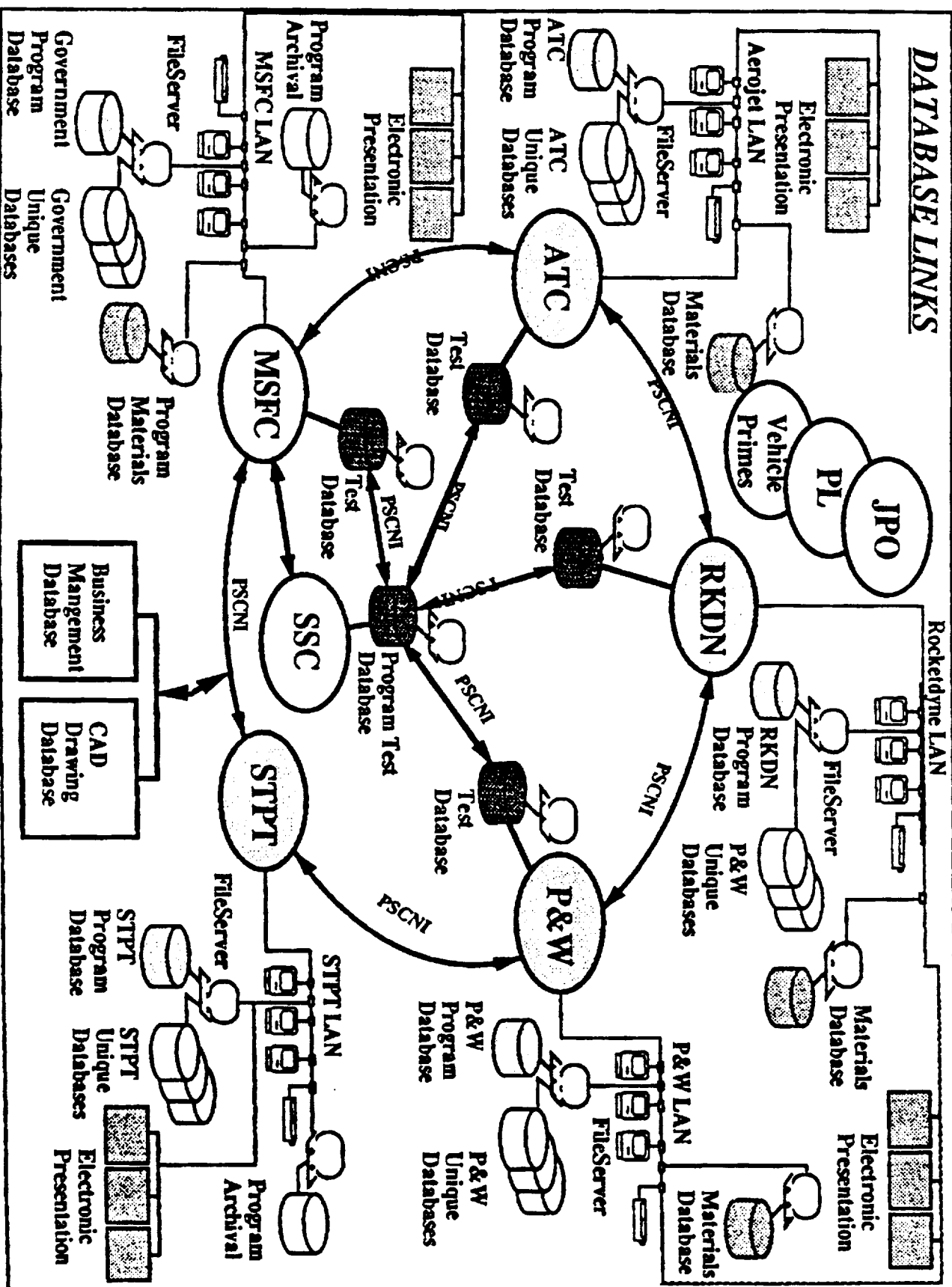
34.	Type of test	Alpha-numeric string
35.	ASTM, ISO or other applicable method number	Alpha-numeric string
36.	Date of applicable standard	Year
37.	Surface treatment	Alpha-numeric string
38.	Thermal treatment	Alpha-numeric string
39.	Surface finish	Alpha-numeric string
40.	Surface residual stress	MPa (ksi)
41.	Data source identification	Alpha-numeric string
42.	Comments(chemistry anomalies, microstructure, etc)	Alpha-numeric string
	Is gage length 4D or 5D	Alpha-numeric string
	Is surface of gage length machined satisfactorily?	Alpha-numeric string

ENVIRONMENT

43.	Test date	Month-year
44.	Test temperature	Degrees C (degrees F)
45.	Method of heating	Alpha-numeric string
46.	Thermocouple location	Alpha-numeric string
47.	Time allocated to reach equilibrium	Alpha-numeric string
48.	Environment (medium)	Alpha-numeric string
49.	Pressure	MPa (psi)
50.	Chemical comp. of medium (MIL-P-27201B)	Alpha-numeric string
51.	Gas analysis method	Alpha-numeric string
52.	Pressure vessel size	Alpha-numeric string
53.	Load cell location	Alpha-numeric string
54.	Humidity of medium	%
55.	Laboratory temperature	Degrees C (degrees F)
56.	Laboratory humidity	%
57.	Method to measure speed of loading to yield (Table T5)	Table T5
58.	Method to measure speed of loading from yield to to fracture (Table T5)	Table T5
59.	Rate of loading (straining) to yield (Table T5)	Table T5
60.	Rate of loading (straining) from yield to fracture (Table T5)	Table T5
61.	Type extensometer	Alpha-numeric string
62.	Method of extensometer attachment	Alpha-numeric string
63.	Class of extensometer	Alpha-numeric string
64.	Extensometer gage length	mm (in)
65.	Method of elongation determination (Table T6)	Alpha-numeric string
66.	Test machine identification	Alpha-numeric string
67.	Load range	N (lbf)
68.	Comments	Alpha-numeric string
69.	Has uniaxial load compensation been made due to pressure?	Alpha-numeric string
70.	Has high pressure data been reported as the effective stress for plastic flow?	Alpha-numeric string
	Is testing speed < 12 MPa/sec (100 ksi/min) or 0.01 mm/mm/sec (0.5 in/in/min)	Alpha-numeric string
	Are temperature tolerances satisfactory?	Alpha-numeric string

NLS PROGRAM

DATABASE LINKS





How a Materials Software System Can Help

- Eliminates Material Test Duplication
- Simplifies Data Reduction
- Speeds Process of Developing Design Allowables
- Capture Pedigree of Materials
- Access On-Line Handbooks and Producers Data
- Qualified Materials Properties are Available to Analysis and Design Groups
- Enables Concurrent Engineering



522 West Laurel Court
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(303) 666-4811 FAX (303) 666-4812

Curt J. Loomis
Sales Manager
Materials Software Operating Group

M/VISION



APPENDIX E

CINDY UPTON

HPLC Test For Resin Advancement

The following High Performance Liquid Chromatography (HPLC) test method was developed at Marshall Space Flight Center (MSFC). Most of the work was done by Ron Sutton of the Chromatography Institute and Bill Cooley of Thiokol (Huntsville Space Operations).

This is a preliminary test method. We still need to further optimize the baseline and peak separations. We found that the THF should be fresh and the water extremely pure (Type 1 - deionized, distilled, filtered through activated charcoal and organic filters).

We also have approximately 20 model compounds and raw constituent materials to run for peak qualification. Currently two methods, each using a two solvent gradient system and reverse phase C-18 columns are under consideration. Once the separation is optimized, individual peaks can be further analyzed by switching to isocratic conditions and a refractive index detector.

Please try out the following HPLC methods in your own laboratory on neat resin and extracted resin, and whatever else you deem appropriate. If you have any questions or comments about this topic, please call Cindy Upton at (205) 544-5755.

HPLC GRADIENT PROFILES

A H₂O
B Methanol
C Acetonitrile
D THF

TABLE #1

Time	Flow	%A	%B
--	2.00	90	10
14.00	2.00	35	65
20.00	2.00	25	75
25.00	2.00	0	100
30.00	2.00	0	100
32.00	2.00	90	10

TABLE #5

Time	Flow	%A	%D
--	2.00	90	10
14.00	2.00	35	65
20.00	2.00	25	75
25.00	2.00	0	100
30.00	2.00	0	100
32.00	2.00	90	10

TABLE #2

Time	Flow	%A	%D
--	2.00	100	0
25.00	2.00	0	100
30.00	2.00	0	100
32.00	2.00	100	0

TABLE #6

Time	Flow	%A	%D
--	2.00	100	0
25.00	2.00	0	100
30.00	2.00	0	100
32.00	2.00	100	0

TABLE #3

Time	Flow	%A	%B
--	1.00	90	10
10.00	1.00	90	10

TABLE #7

Time	Flow	%A	%D
30.00	1.00	0	100

TABLE #4

Time	Flow	%A	%C
--	2.00	90	10
14.00	2.00	35	65
20.00	2.00	25	75
25.00	2.00	0	100
30.00	2.00	0	100
32.00	2.00	90	10

MEASUREMENT CONDITIONS
 < FILE No.: C FILE NAME: BILL DATE :Apr/30/92 >

KEY LOCK : OFF
 INTERVAL : NORMAL
 TIME CONSTANT : 2.0 sec
 MEASUREMENT TIME : 30.00 min
 DISPLAY TIME : 30.00 min
 WAVELENGTH RANGE : 210 --- 400 nm
 WAVELENGTH : 215 280 300 334 nm
 BAND WIDTH : 5 5 5 5 nm

MEASUREMENT CONDITIONS
 < FILE No.: C FILE NAME: BILL DATE :Apr/30/92 >

KEY LOCK : OFF
 INTERVAL : NORMAL
 TIME CONSTANT : 2.0 sec
 MEASUREMENT TIME : 30.00 min
 DISPLAY TIME : 30.00 min
 WAVELENGTH RANGE : 210 --- 400 nm
 WAVELENGTH : 215 280 300 334 nm
 BAND WIDTH : 5 5 5 5 nm

CH: 1 CHROMATOGRAM CONDITIONS
 < FILE No.: C FILE NAME: BILL DATE :Apr/30/92 >

TIME (min)	AUFS (AU)	WAVELENGTH (nm)	W.PLOT	EVENT	THRESHOLD
INITIAL	0.500	215	OFF	OFF	

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CH: 2 CHROMATOGRAM CONDITIONS
 < FILE No.: C FILE NAME: BILL DATE :Apr/30/92 >

TIME (min)	AUFS (AU)	WAVELENGTH (nm)	W.PLOT	EVENT	THRESHOLD
INITIAL	0.500	280	OFF	OFF	

CH: 3 CHROMATOGRAM CONDITIONS
 < FILE No.: C FILE NAME: BILL DATE : Apr/30/92 >
 TIME AUFS WAVELENGTH W.PLOT EVENT THRESHOLD
 (min) (AU) (nm)

 INITIAL 0.100 215 OFF OFF

CH: 4 CHROMATOGRAM CONDITIONS
 < FILE No.: C FILE NAME: BILL DATE : Apr/30/92 >
 TIME AUFS WAVELENGTH W.PLOT EVENT THRESHOLD
 (min) (AU) (nm)

 INITIAL 0.100 300 OFF XXXX

31220 9021

Waters

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31220 9021

Water

SPECTRUM CONDITIONS < MONITOR: M1 >
< FILE No.: C FILE NAME: BILL DATE :Apr/30/92 >
TIME HEIGHT SLOPE NOISE MODE MONITOR WAVE.
(min) (AU) (AU/min) (AU) (nm)

INITIAL 0.0051 0.001 1.0E-04 P/S/V 215

ANALYSIS MENU
< FILE No.: C FILE NAME: BILL DATE :Apr/30/92 >
===== < INTEGRATOR >===== PLOT : OFF

TIME RANGE : 0.00 --- 30.00 min
WAVELENGTH : M1
SMOOTHING : 7 points
SLOPE : 0.001 AU/min
DRIFT : 0.001 AU/min
HEIGHT : 0.001 AU
WIDTH : 0.01 min
TIME DOUBLE : 183 min
MINIMUM AREA : 0.001 AU*min
MINUS PEAK : OFF
PAPER SPEED : 10.0 mm/min
BASELINE CORRECT : OFF
CALIBRATION : OFF

ANALYSIS MENU
< FILE No.: C FILE NAME: BILL DATE :Apr/30/92 >
===== < SPECTRUM INDEX >===== PLOT : OFF

TIME RANGE : 0.00 --- 30.00 min
WAVELENGTH RANGE : 210 --- 400 nm
SPECTRUM CORRECT : ON
SPECTRUM SCALE : AUTO SCALE
BASELINE CORRECT : 0.00 --- 30.00 min
CHROMATOGRAM : M1

ANALYSIS MENU
< FILE No.: C FILE NAME: BILL DATE :Apr/30/92 >
===== < CHROMATOGRAM >===== PLOT : ON

TIME RANGE : 0.00 --- 30.00 min
SCALE M1 : AUTO SCALE
M2 : AUTO SCALE
PLOT SPEED : 10.0 mm/min
BASELINE CORRECT : 0.00 --- 30.00 min
CHROMATOGRAM : M1 & M2

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STORED
< FILE No.: C FILE NAME: BILL DATE :Apr/30/92 >

M1 : ON M2 : ON

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Water

31220 9021

MEASUREMENT COMMENT
< FILE No.: C FILE NAME: BILL DATE :Apr/30/92 >

SAMPLE NAME : WATER/THF BLANK
COLUMN : 3.9mmID* 15.0cm
PACKING MATERIAL : C-18
MOBILE PHASE : H2O-THF GRADIENT
FLOW RATE : 2.00 ml/min
PRESSURE : 0.0 PSI
TEMPERATURE : 25.0 °C
INJECTION VOLUME : 10 µl

MEASUREMENT CONDITIONS
< FILE No.: 2 FILE NAME: RON DATE :Apr/27/92 >

KEY LOCK : OFF
INTERVAL : NORMAL
TIME CONSTANT : 2.0 sec
MEASUREMENT TIME : 30.00 min
DISPLAY TIME : 30.00 min
WAVELENGTH RANGE : 220 --- 400 nm
WAVELENGTH : 270 280 300 334 nm
BAND WIDTH : 5 5 5 5 nm

CH: 1 CHROMATOGRAM CONDITIONS
< FILE No.: 2 FILE NAME: RON DATE :Apr/27/92 >
TIME AUFS WAVELENGTH W.PLOT EVENT THRESHOLD
[min] [AU] [nm]

INITIAL 0.500 280 OFF OFF

CH: 2 CHROMATOGRAM CONDITIONS
< FILE No.: 2 FILE NAME: RON DATE :Apr/27/92 >
TIME AUFS WAVELENGTH W.PLOT EVENT THRESHOLD
[min] [AU] [nm]

INITIAL 0.100 270 OFF OFF

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OF POOR QUALITY

CH: 3 CHROMATOGRAM CONDITIONS
< FILE No.: 2 FILE NAME: RON DATE :Apr/27/92 >
TIME AUFS WAVELENGTH W.PLOT EVENT THRESHOLD
[min] [AU] [nm]

INITIAL 0.100 270 OFF OFF

CH: 4 CHROMATOGRAM CONDITIONS
< FILE No.: 2 FILE NAME: RON DATE :Apr/27/92 >
TIME AUFS WAVELENGTH W.PLOT EVENT THRESHOLD
(min) (AU) (nm)

INITIAL 0.100 300 OFF XXX

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OF POOR QUALITY

Waters

SPECTRUM CONDITIONS < MONITOR: M1 >
 < FILE No.: 2 FILE NAME: RON DATE :Apr/27/92 >
 TIME HEIGHT SLOPE NOISE MODE MONITOR WAVE.
 [min] [AU] [AU/min] [AU] [nm]

 INITIAL 0.0051 0.001 1.0E-04 P/S/V 280

31220 9021

ANALYSIS MENU
 < FILE No.: 2 FILE NAME: RON DATE :Apr/27/92 >
 =====< INTEGRATOR >===== PLOT : ON
 TIME RANGE : 0.00 --- 30.00 min
 WAVELENGTH : M1
 SMOOTHING : 7 points
 SLOPE : 0.001 AU/min
 DRIFT : 0.001 AU/min
 HEIGHT : 0.001 AU
 WIDTH : 0.01 min
 TIME DOUBLE : 183 min
 MINIMUM AREA : 0.001 AU*min
 MINUS PEAK : OFF
 PAPER SPEED : 10.0 mm/min
 BASELINE CORRECT : OFF
 CALIBRATION : OFF

Waters

ANALYSIS MENU
 < FILE No.: 2 FILE NAME: RON DATE :Apr/27/92 >
 =====< SPECTRUM INDEX >=== PLOT : ON
 TIME RANGE : 0.00 --- 30.00 min
 WAVELENGTH RANGE : 220 --- 400 nm
 SPECTRUM CORRECT : ON
 SPECTRUM SCALE : AUTO SCALE
 BASELINE CORRECT : OFF
 CHROMATOGRAM : M1

ANALYSIS MENU
 < FILE No.: 2 FILE NAME: RON DATE :Apr/27/92 >
 =====< CHROMATOGRAM >===== PLOT : ON
 TIME RANGE : 0.00 --- 30.00 min
 SCALE M1 : AUTO SCALE
 M2 : AUTO SCALE
 PLOT SPEED : 10.0 mm/min
 BASELINE CORRECT : OFF
 CHROMATOGRAM : M1 & M2

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STORED
 < FILE No.: 2 FILE NAME: RON DATE :Apr/27/92 >

 M1 : ON M2 : ON

0-3

SAMPLE NAME : 91LD IN MEOH
COLUMN : 3.9mmID* 15.0cm
PACKING MATERIAL : C-18
MOBILE PHASE : H2O-MEOH GRADIENT
FLOW RATE : 2.00 ml/min
PRESSURE : 0.0 PSI
TEMPERATURE : 25.0 °C
INJECTION VOLUME : 20 µl

Waters

31220 9021

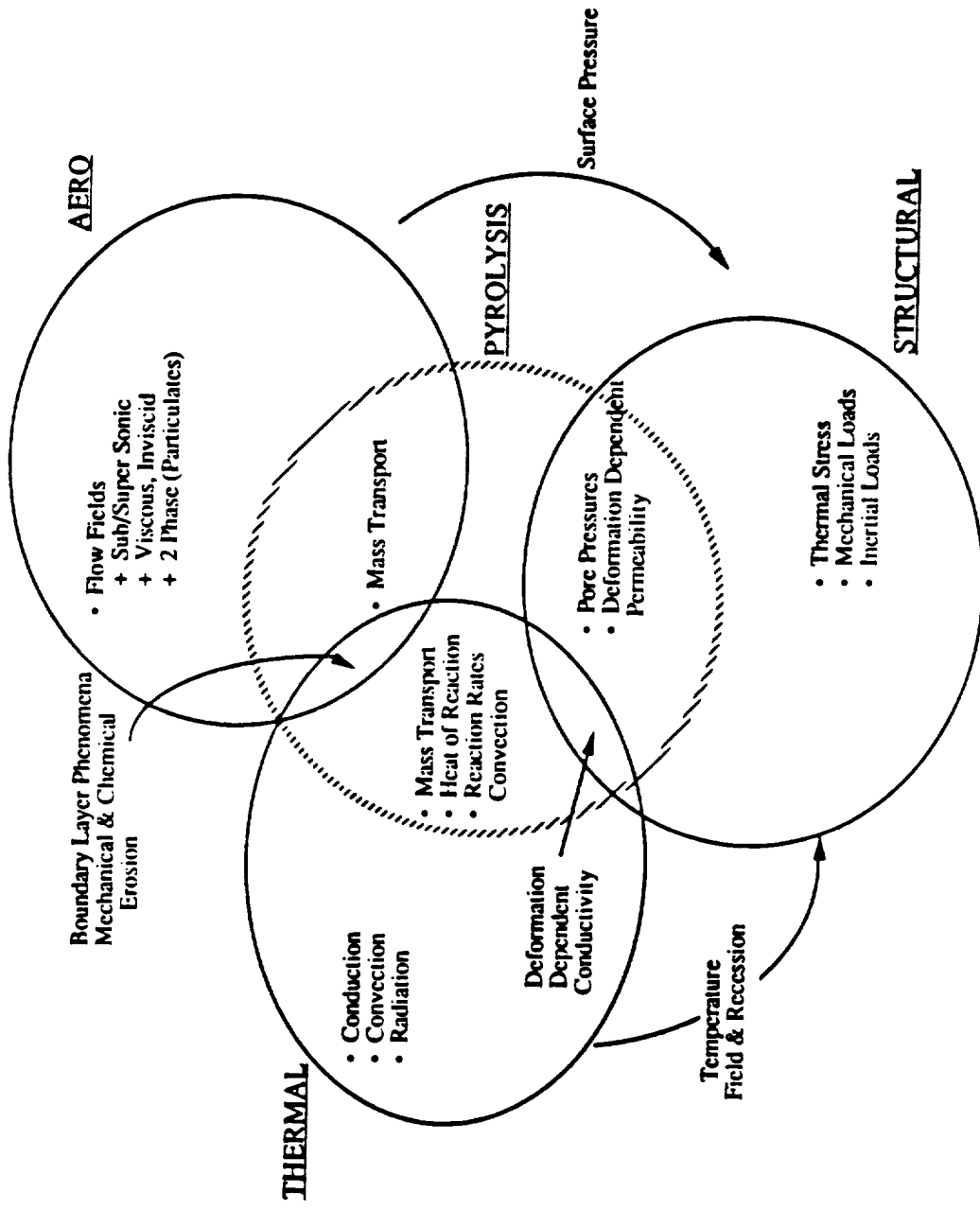
Waters

31220 9021

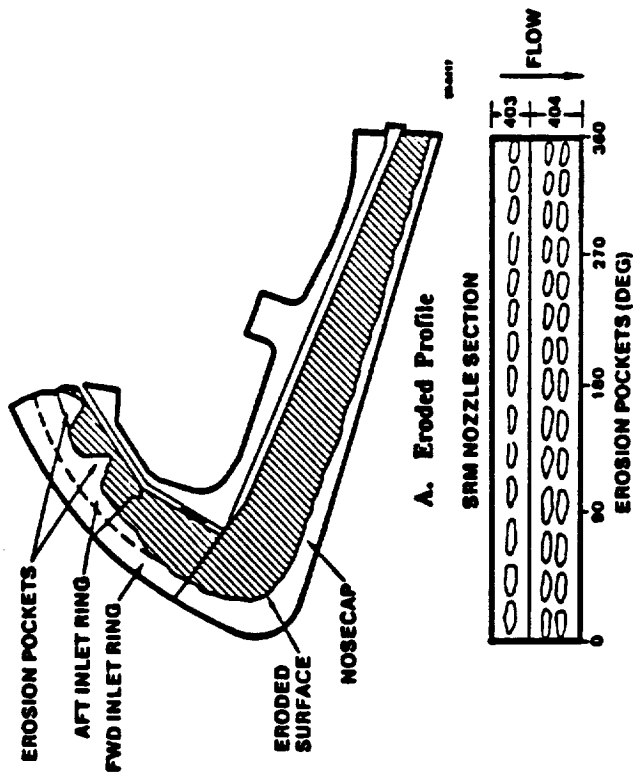
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APPENDIX F
GREG CROSE

AERO-THERMAL-STRUCTURAL ANALYSIS

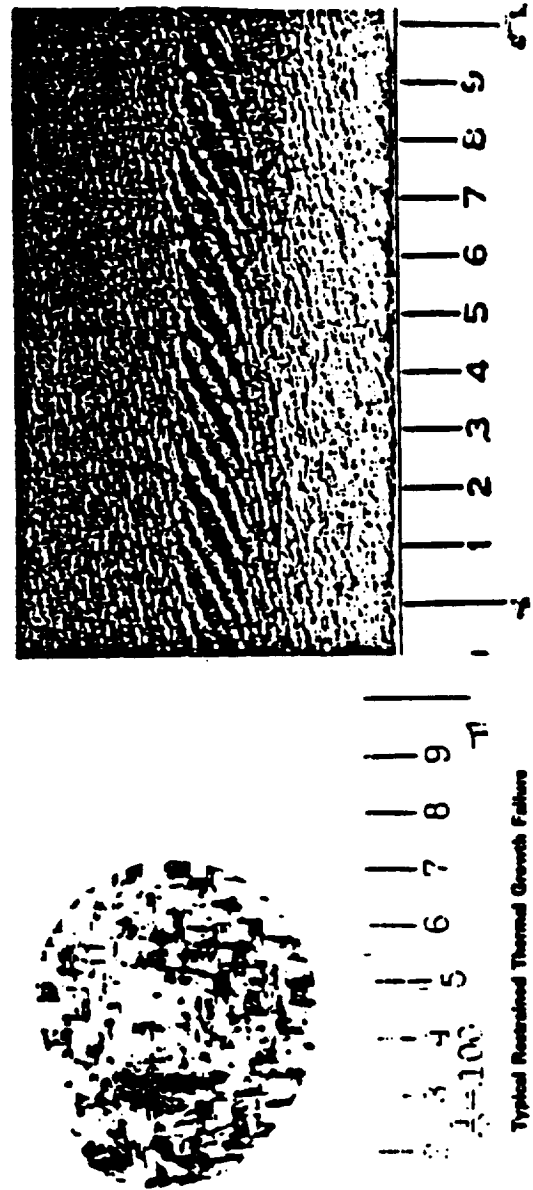


SRM PROBLEM AREAS



B. Crack At Base Of Erosion Pit

ANOMALOUS EROSION OF SRM

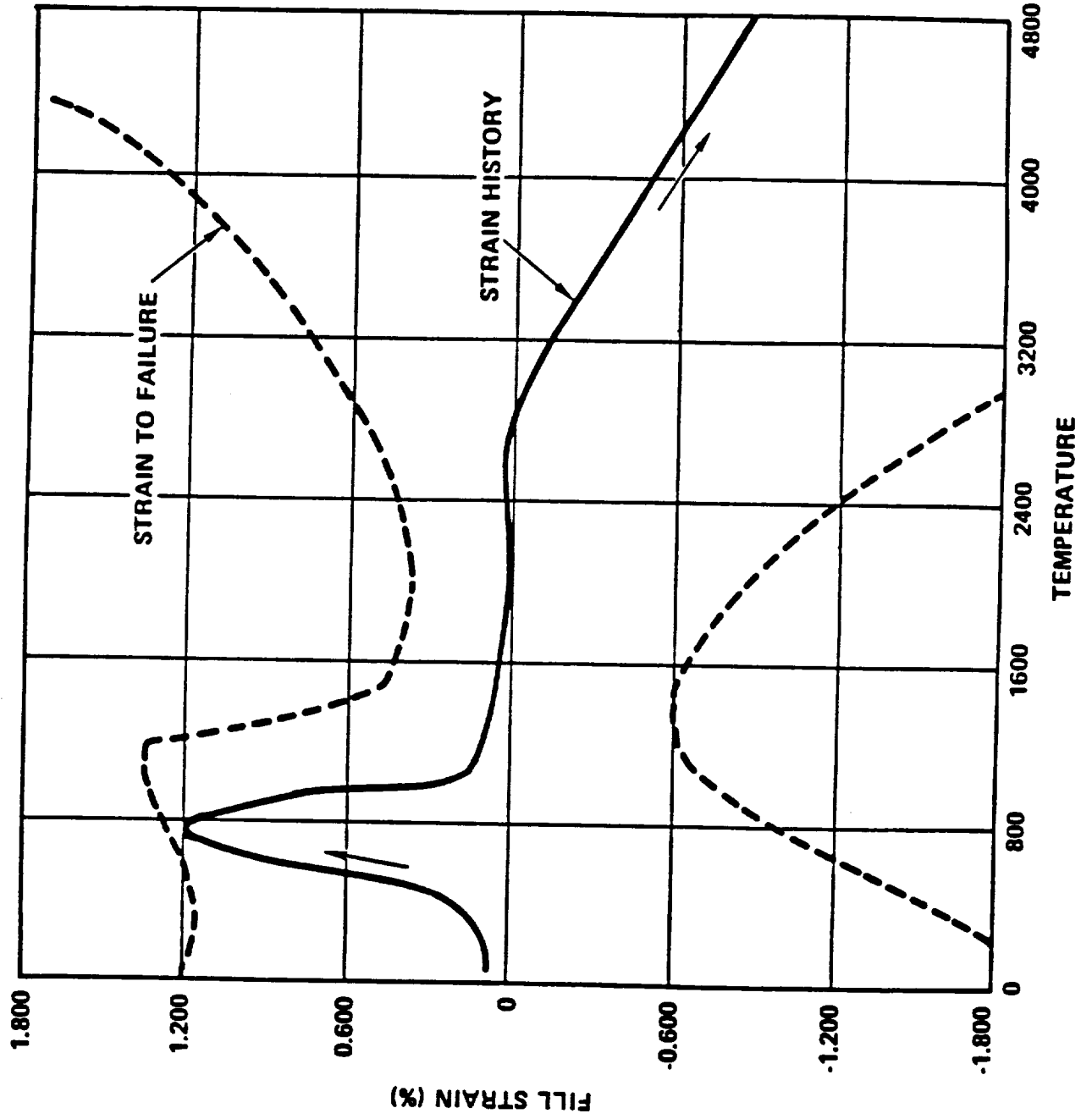


Typical Restricted Thermal Growth Failure

LABORATORY EVIDENCE OF FIBER FAILURE
DUE TO RESTRAINT OF EXPANSION

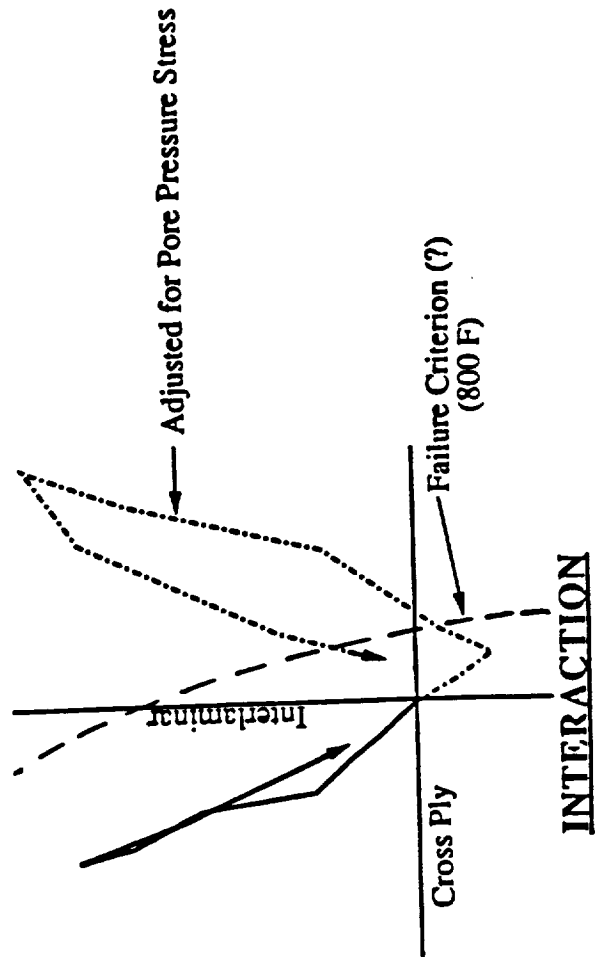
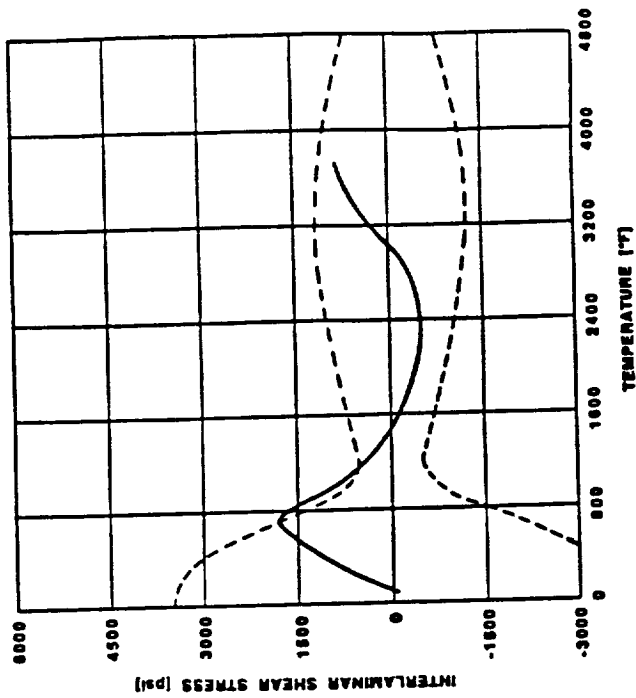
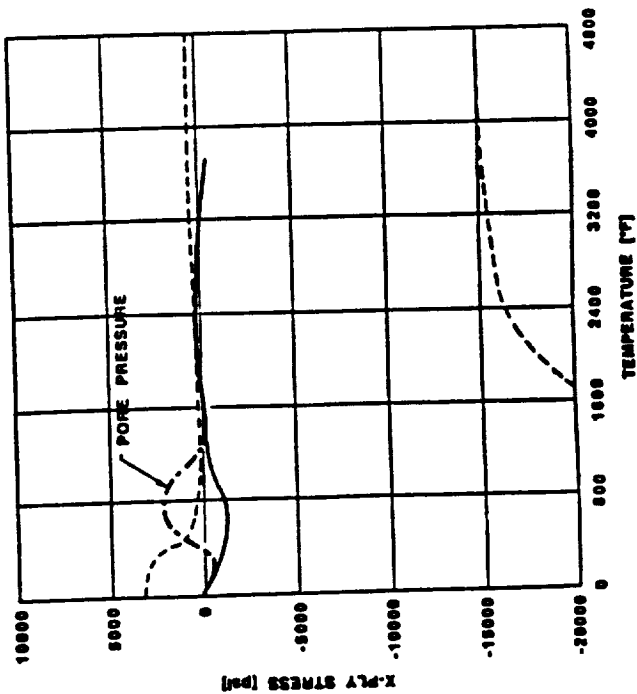
PLY LIFT

STRESS-STRAIN STATE ASSOCIATED WITH POCKETING CASE 1A

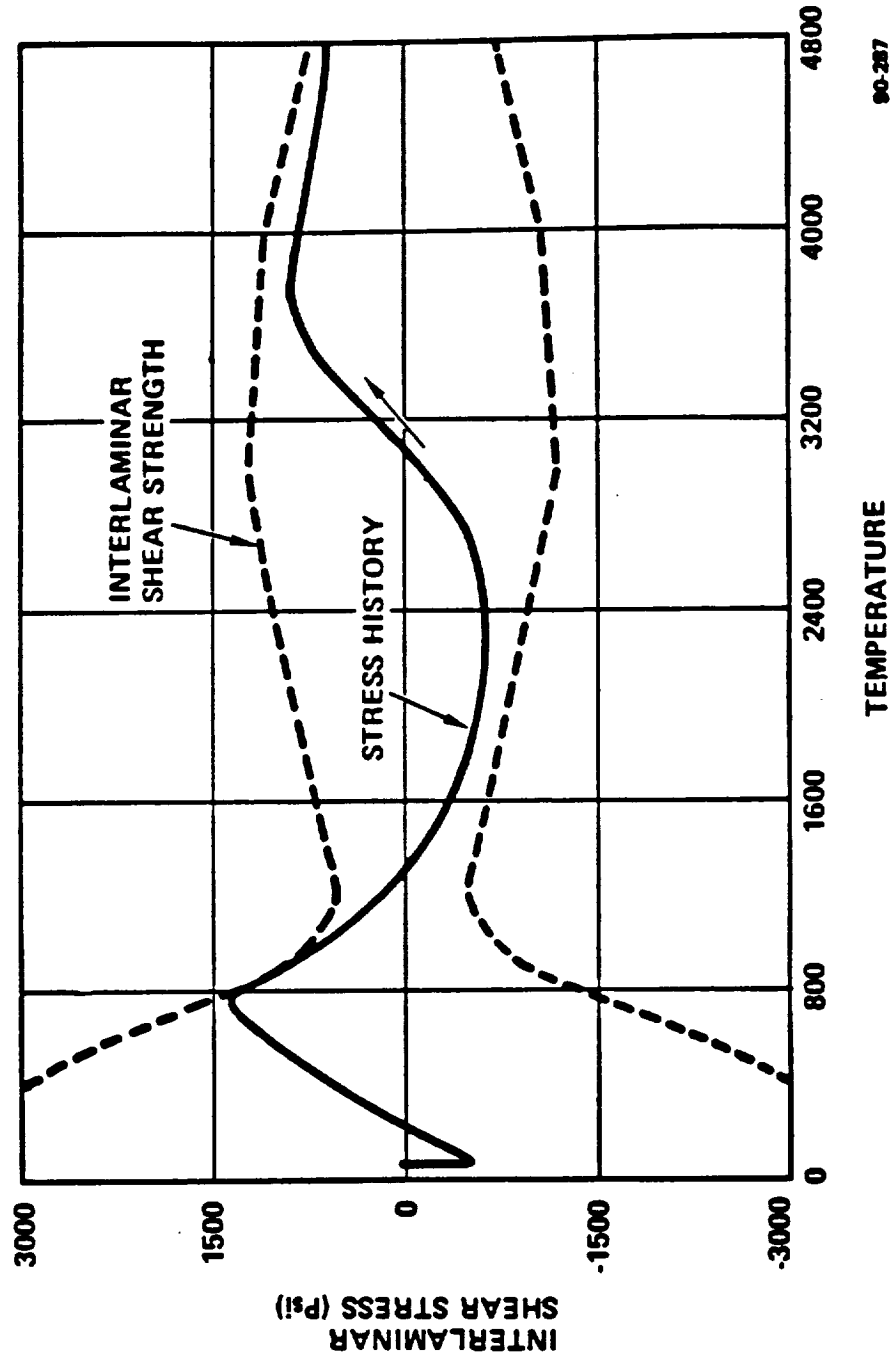




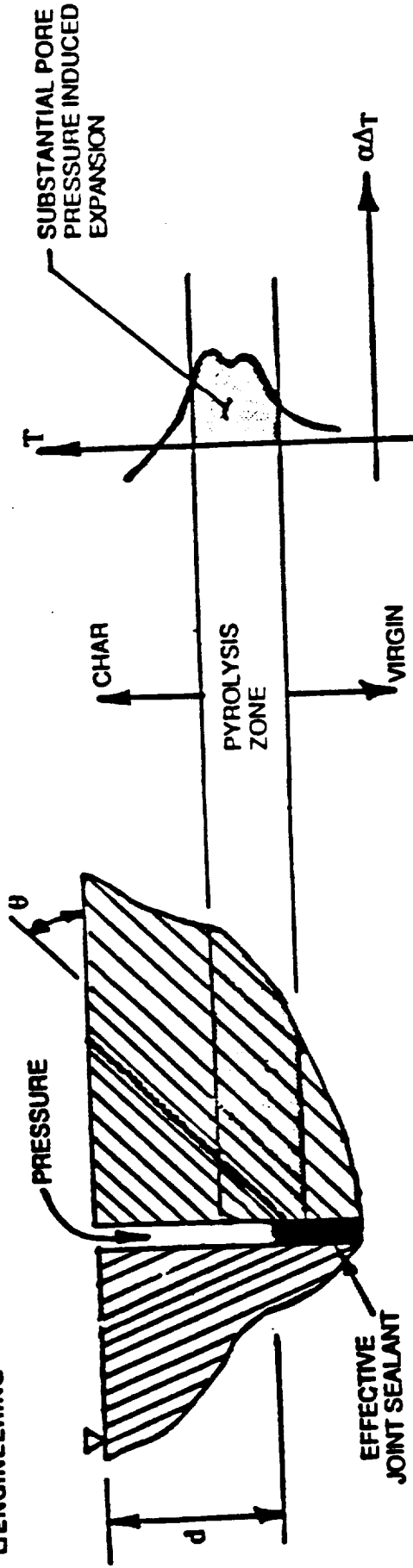
STRESS-STRAIN STATE ASSOCIATED WITH PLY LIFT CASE III



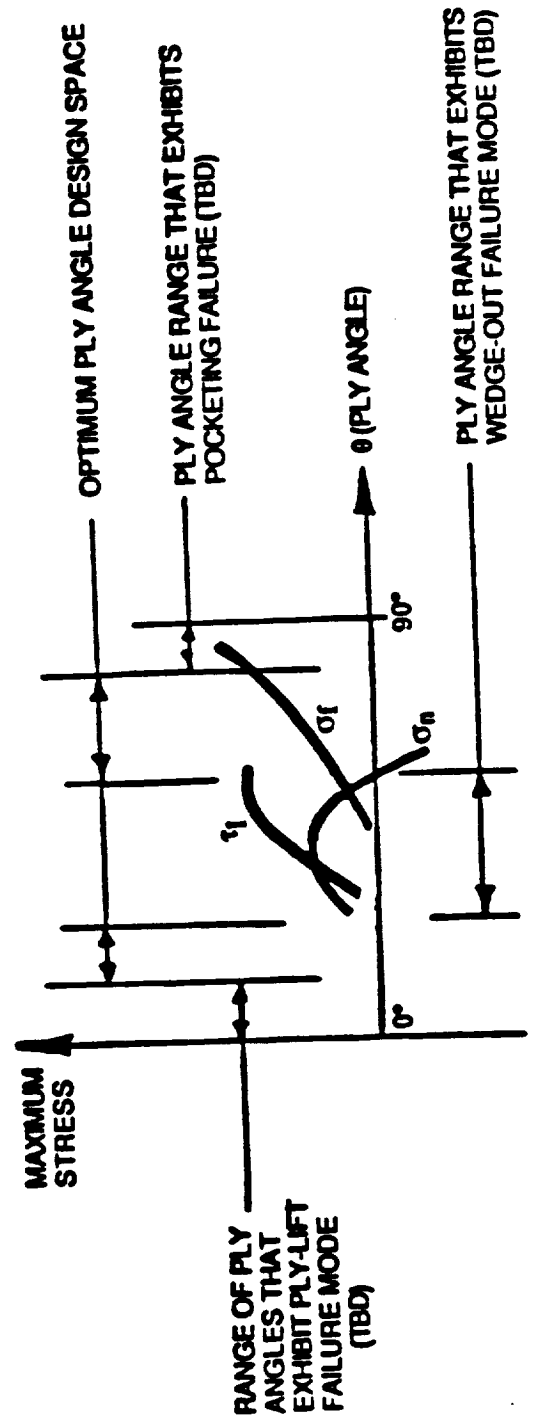
STRESS-STRAIN STATE ASSOCIATED WITH WEDGE OUT CASE IIB



WEDGE OUT FAILURE MODE

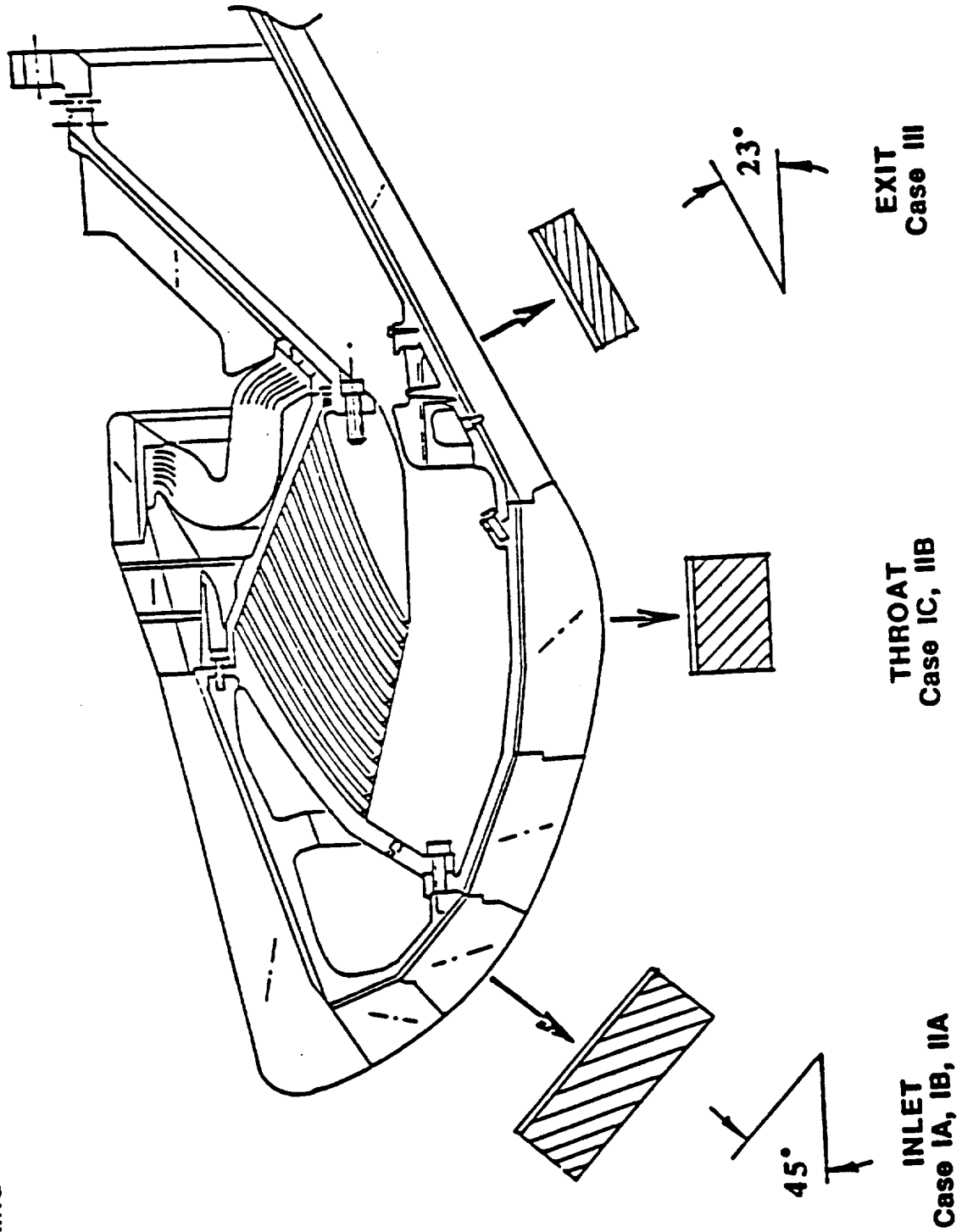


OVERALL FAILURE ISSUE

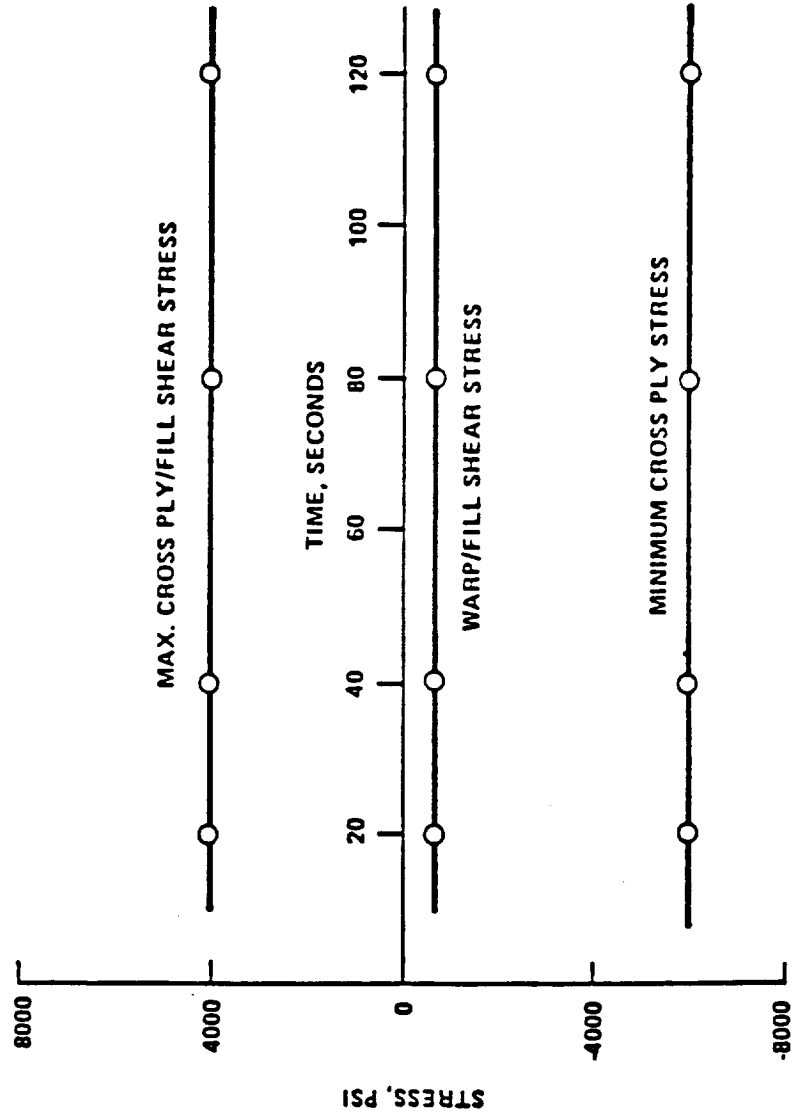


ANALYSIS SENSITIVITIES

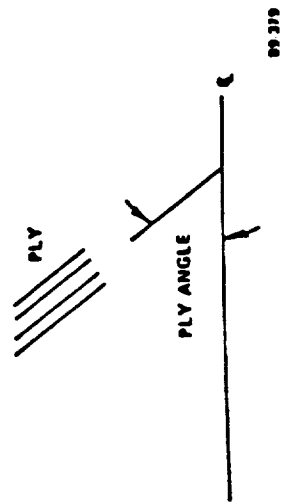
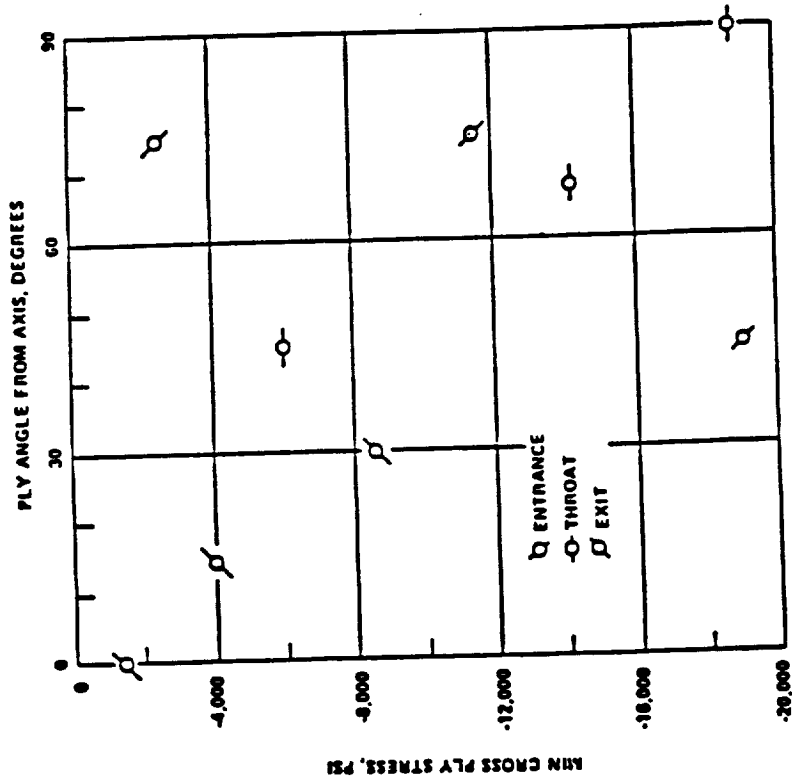
NOZZLE SCALE STUDY ANALYSIS LOCATIONS



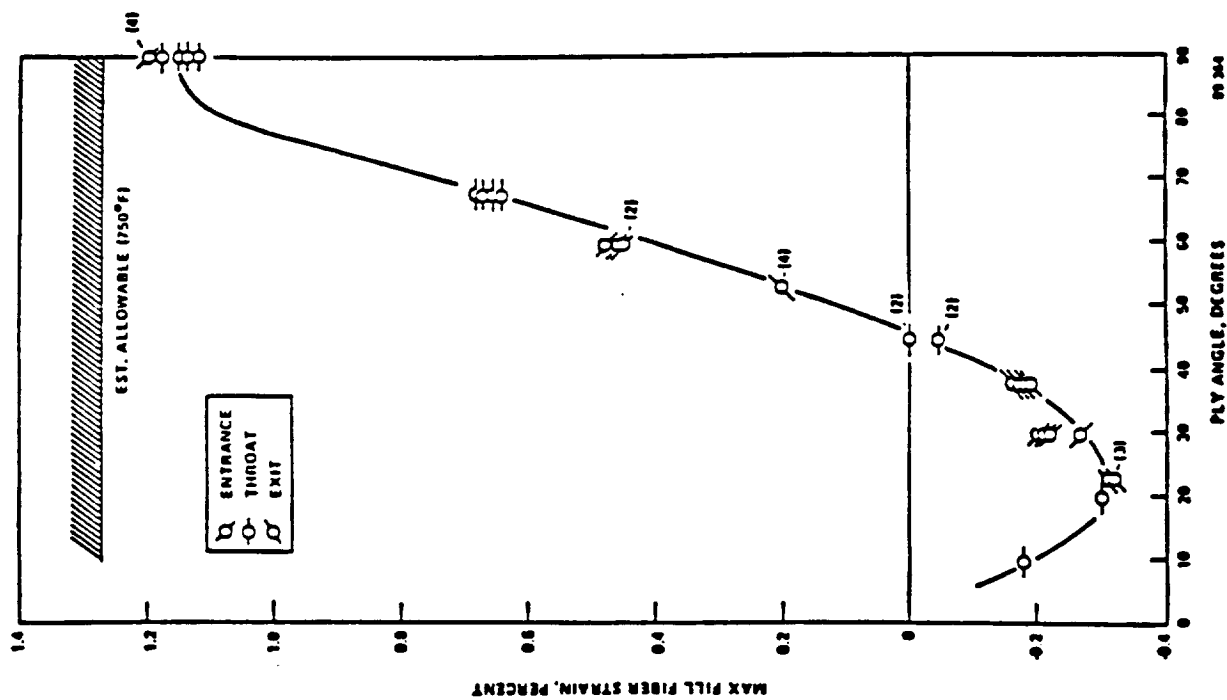
CRITICAL STRESS HISTORIES - 54-INCH NOZZLE THROAT WITH 45° PLY ANGLE



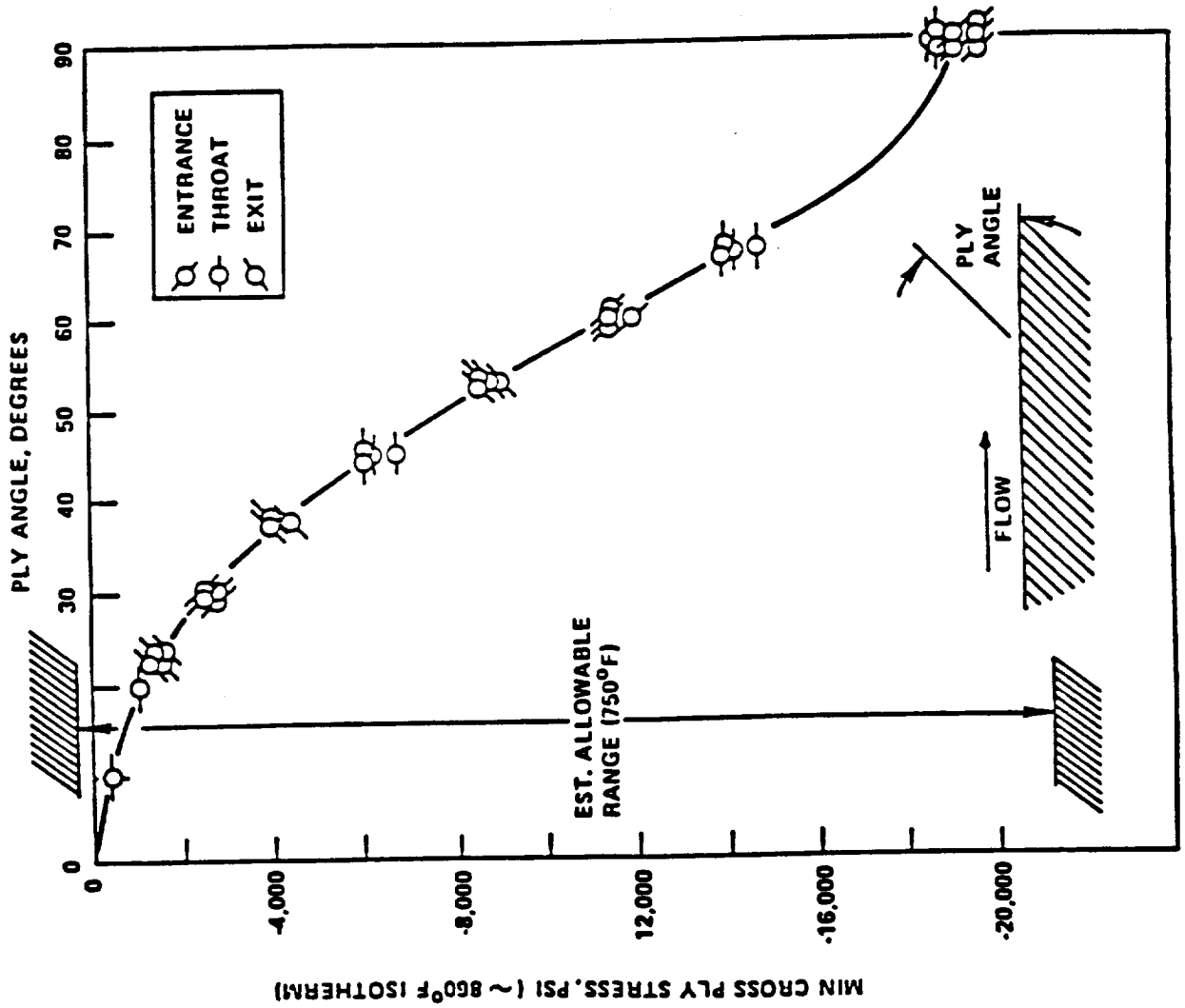
CRITICAL CROSS-PLY STRESSES VS. PLY ANGLE RELATIVE TO THE NOZZLE AXIS



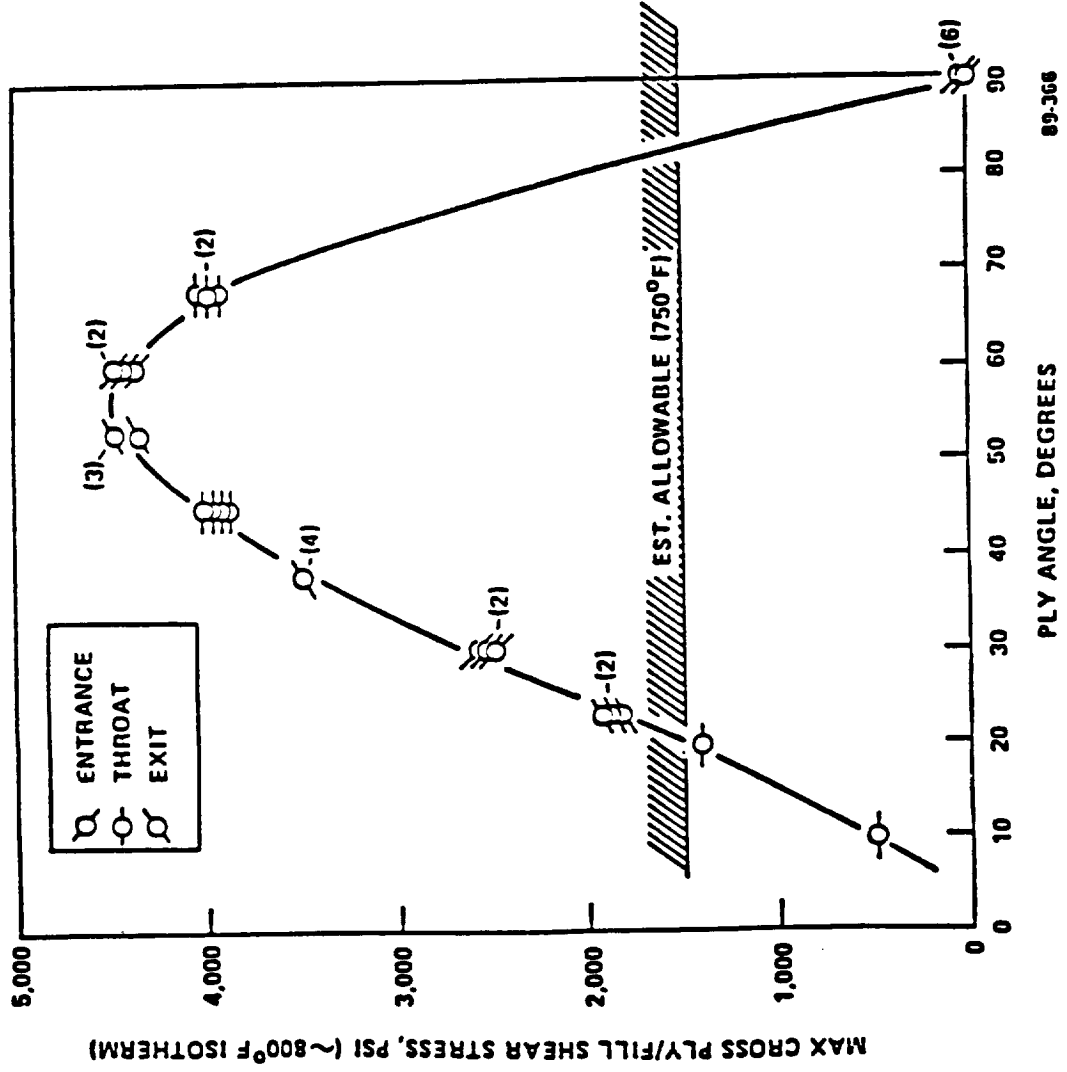
MAXIMUM FILL FIBER STRAIN VS. PLY ANGLE RELATIVE TO THE HOT SURFACE



CRITICAL CROSS-PLY STRESSES VS. PLY ANGLE RELATIVE TO THE HOT SURFACE



MAXIMUM CROSS-PLY FILL SHEAR STRESS VS. PLY ANGLE RELATIVE TO THE HOT SURFACE



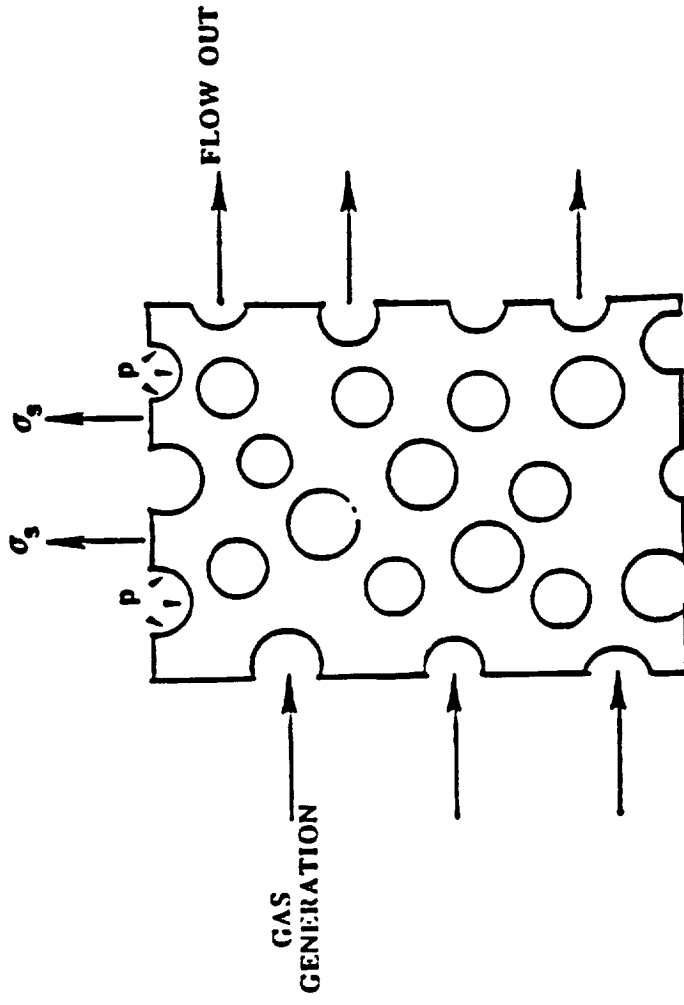
SCALING STUDY CONCLUSIONS - FM5055 CARBON-PHENOLIC, SRM CHAMBER PRESSURE, GEOMETRY

- Predicted char/erosion greater in subscale motors.
- Predicted char thickness increases with time similarly in all size motors.
- Very little difference in thermal behavior upstream or downstream of throat.
- Very little effect on thermal stress from:
 - Time of firing
 - Nozzle size
 - Heating rate
- Major determinant of critical stress levels is angle of tapewrap to hot surface.
- Contradictions to above involve phenomena not currently addressed in our codes, e.g.:
 - Coupling of conductivity, permeability, deformation
 - Path length for pyrolysis gases
 - Direction of pyrolysis gas flow
 - Upstream mass addition from pyrolyzing components
 - 3D flow field phenomena
 - Local flow field disturbance

CARBON-PHENOLIC PORE PRESSURE DRIVEN ANALYSES

INTERNAL PORE PRESSURES

- PYROLYSIS GASES FORM DURING BURN, DEVELOP PRESSURE AGAINST RESISTANCE TO FLOW
- PORE PRESSURES LOAD MATERIAL SIMILAR TO THERMAL STRESS
- EFFECTIVE POROSITY NOT EQUAL VOLUME POROSITY
- TREAT MACROSCOPICALLY
- HIGHLY COUPLED BEHAVIOR
 - PERMEABILITY = f (porosity)
 - FLOW = f (PERMEABILITY, \dot{m})
 - PORE PRESSURE = f (FLOW FIELD, \dot{m})
 - DEFORMATION = f (PORE PRESSURE)
 - POROSITY = f (DEFORMATION)



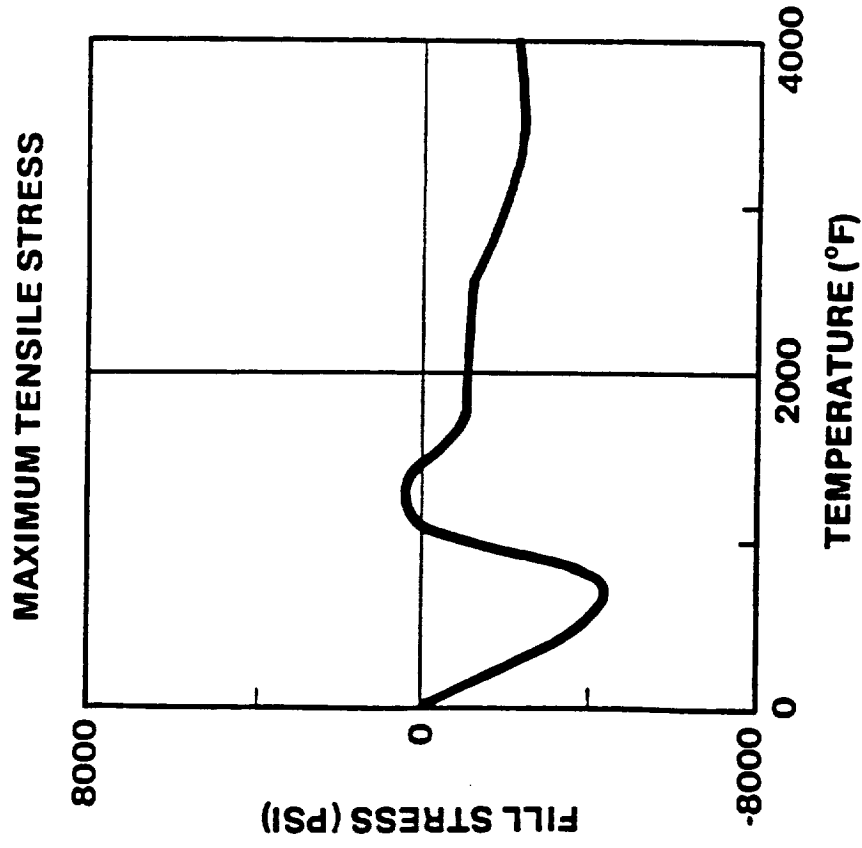
PORE PRESSURE STRESS

$$\sigma_{\Phi} = f_p$$

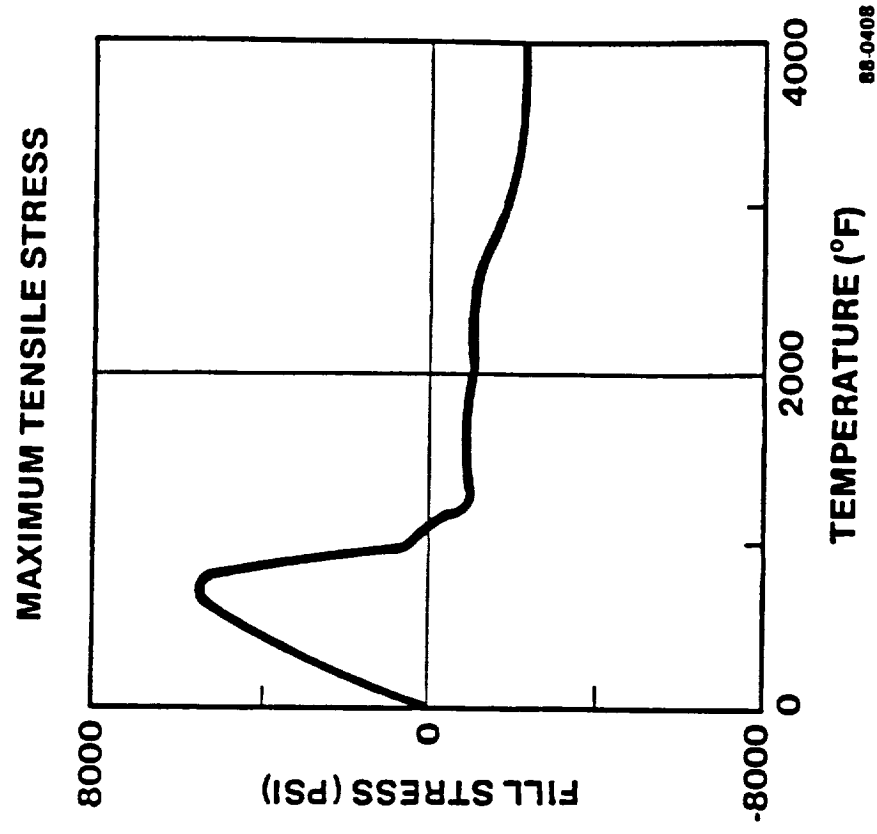
STRESS DEFINITION

$$\sigma_s = F_s / A_{total}$$

THERMAL STRESS IN SRM 403 RING



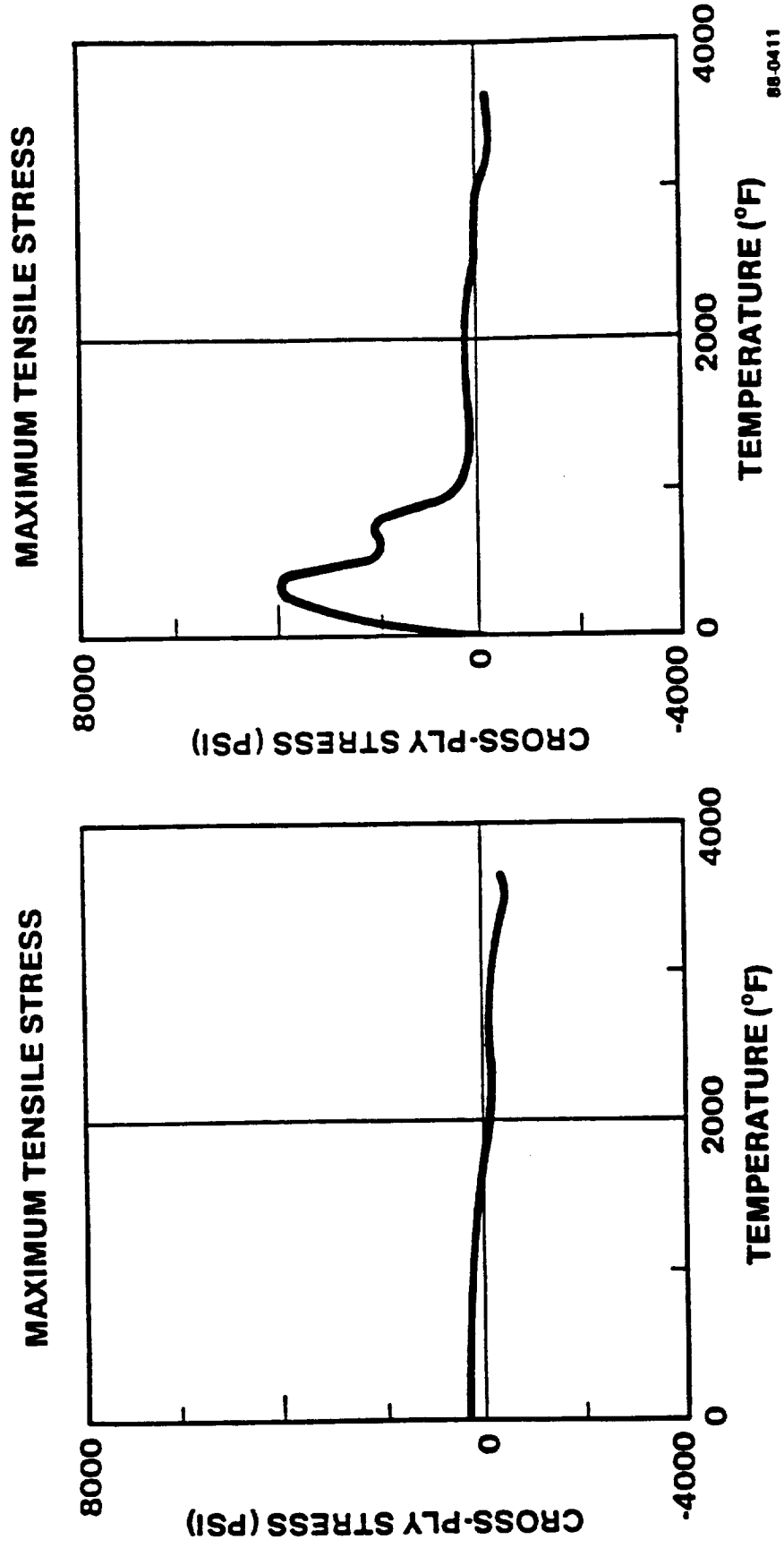
A. Conventional Analysis



B. Pore Pressure Driven Analysis



THERMAL STRESS IN SRM EXIT CONE



A. Conventional Analysis

B. Pore Pressure Driven Analysis

CRITICAL MATERIAL CHARACTERISTICS

- **Moisture Content - Supply of Water/Steam**
- **Permeability - Resistance to Flow**
- **Porosity - Storage for Expanding Gases**
- **Cross-Ply Tensile and Shear Strength and Strain to Failure - Interlaminar Failure**
- **In-Plane Strain to Failure - Accommodate Incompressibility, Fiber Failure**
- **Pore Pressure Potential - Driving Force**
 - **Expansion**
 - **Restrained Growth**
 - **Constituent Chemistry**
- **Crack Propagation - Wedgeout**
 - **Into Virgin Material**
 - **Into Char Material**

APPENDIX G

TOM FISHER

**NMR Studies of Phenol-Formaldehyde Resins
and Their Model Compounds**

Tom H. Fisher

**Department of Chemistry
Mississippi State University**

PROPOSED RESEARCH

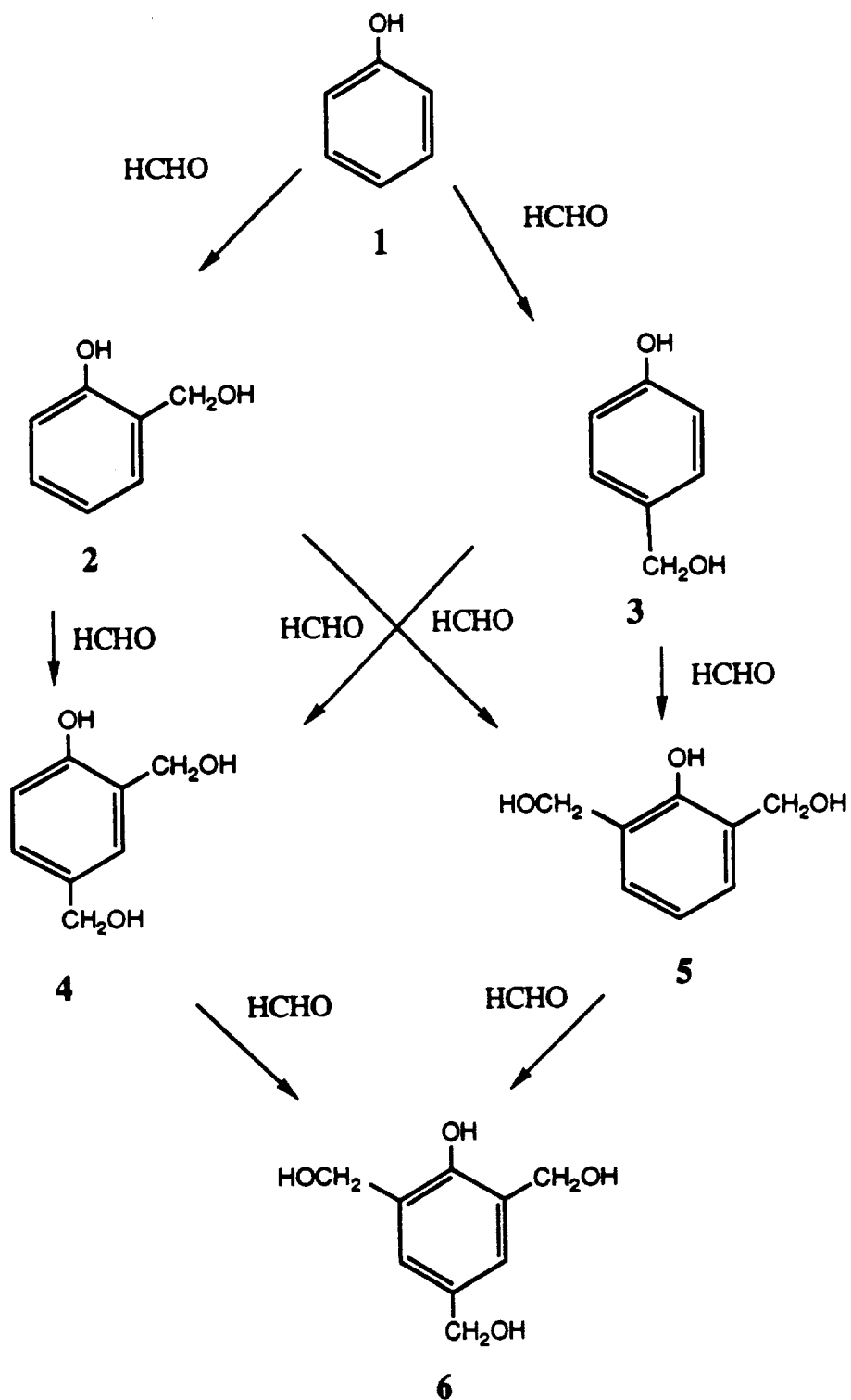
MODEL COMPOUNDS:

- Methylphenols**
- Methylolphenols**
- Hydroxydiphenylmethanes**
- Others**

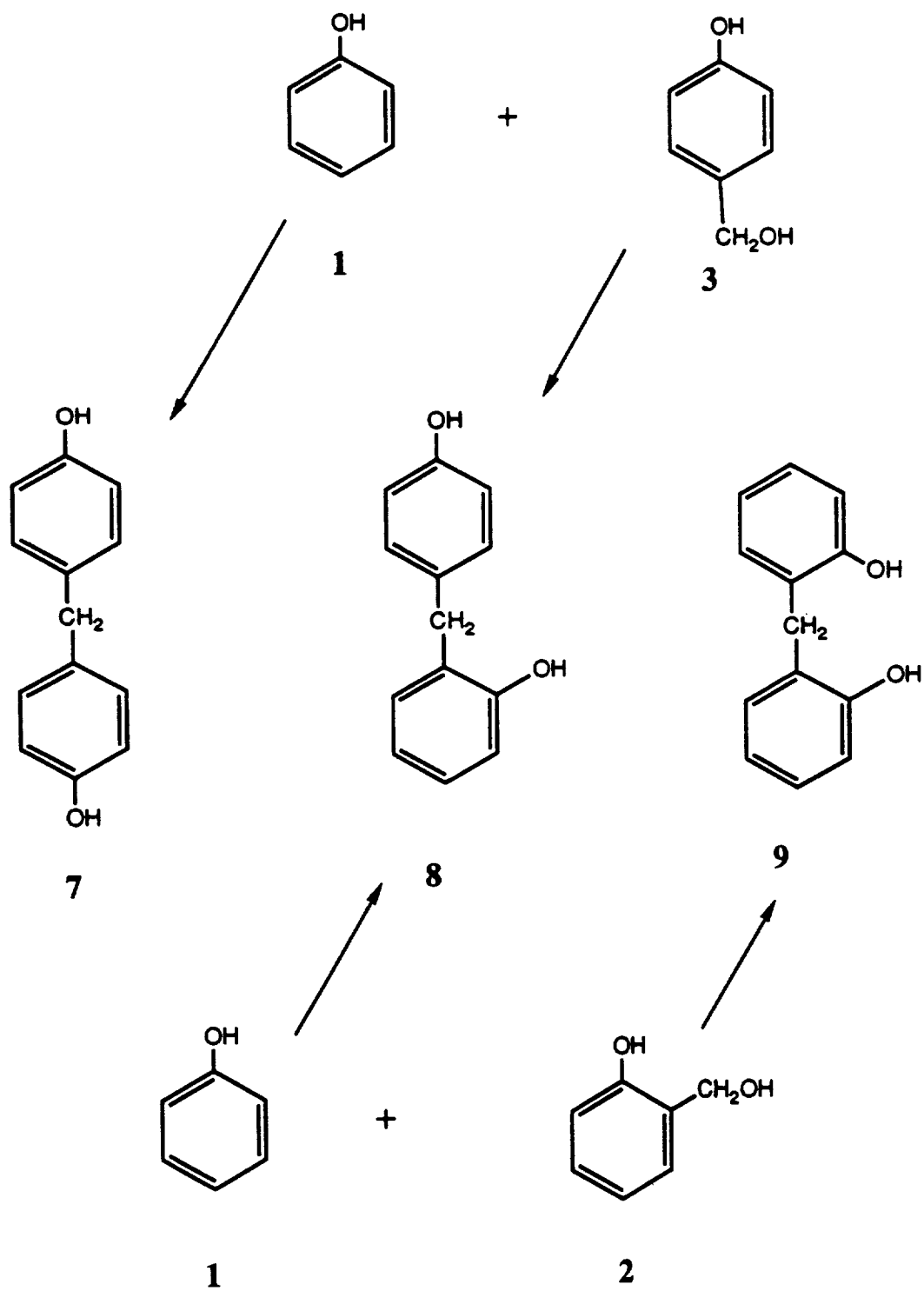
PF RESINS: SC 1008, 91 LD, P 31

- Prepolymer**
- Prepreg resin**
- Various stages of resin advancement cure**
- Cured resin (if get solids probe)**

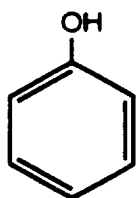
Phenol + Formaldehyde + Base -----> Resol



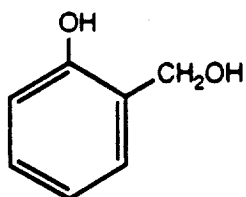
Diarylmethane Formation



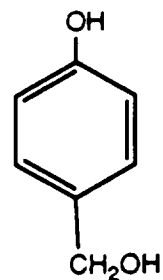
Phenol-Formaldehyde Resin Model Compounds



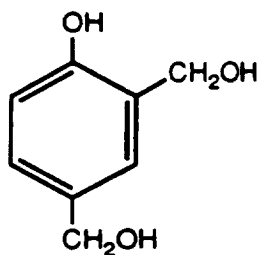
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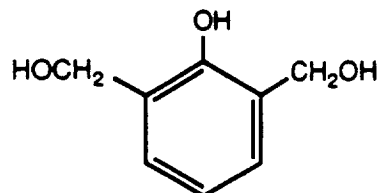
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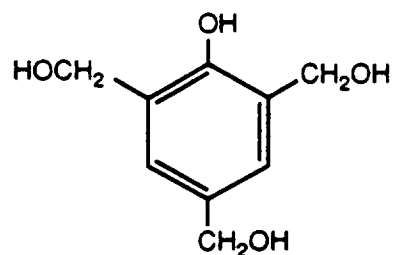
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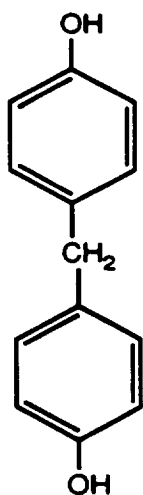
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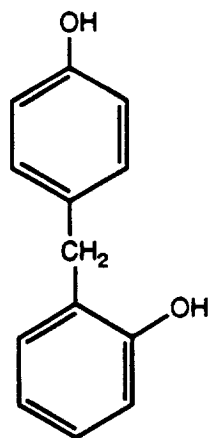
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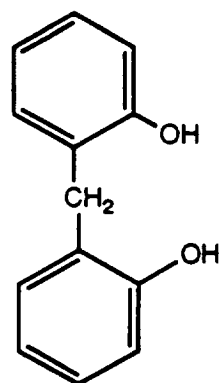
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7

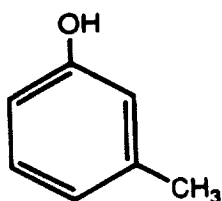


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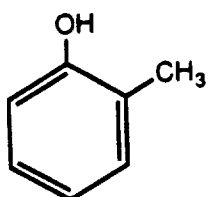


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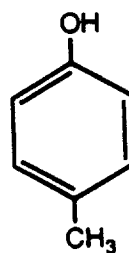
Phenol-Formaldehyde Resin Model Compounds



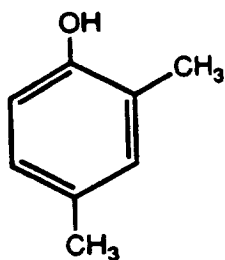
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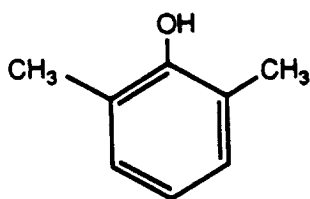
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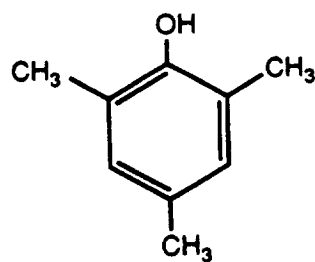
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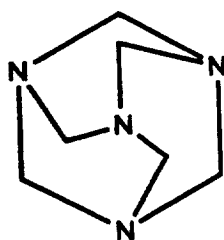
13



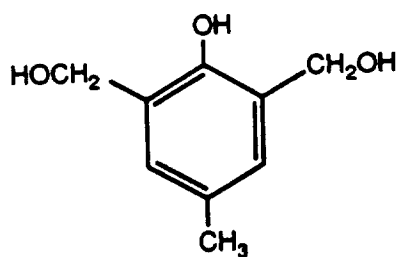
14



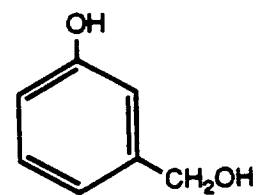
15



16



17



18

HCHO

19

ASSIGNMENTS OF C-13 NMR OF PF MODEL COMPOUNDS

<u>C#</u>	<u>1*</u>	<u>2*</u>	<u>3*</u>	<u>4*</u>	<u>5*</u>	<u>6*</u>
1	158.24	156.15	157.28			
2	116.06	128.14	115.75			
3	130.21	128.39	129.16			
4	120.14	120.11	133.77			
5	130.21	128.82	129.16			
6	116.06	115.99	115.75			
<u>o</u> -R	-	61.86	-			
<u>m</u> -R	-	-	-			
<u>p</u> -R	-	-	64.55			
Other	-	-	-			

<u>C#</u>	<u>7*</u>	<u>8*</u>	<u>8 ('ring')*</u>	<u>9*</u>	<u>10</u>	<u>11</u>
1	133.71	129.26	132.92	128.18	158.21	156.18
2	130.45	155.68	130.62	155.39	116.74	124.91
3	115.93	115.80	116.00	131.35	139.95	131.51
4	156.36	127.82	128.00	120.64	120.94	120.19
5	115.93	120.34	120.64	128.00	129.98	127.5
6	130.45	131.86	131.35	116.00	113.12	115.43
<u>o</u> -R	-	35.39	-	30.48	-	16.14
<u>m</u> -R	-	-	-	-	21.39	-
<u>p</u> -R	40.72	-	(35.39 same)	-	-	-
Other	-	-	-	-	-	-

* present in PF resin

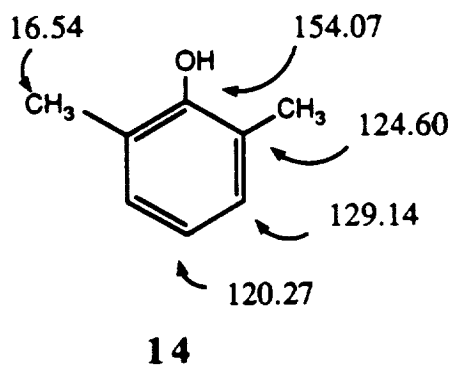
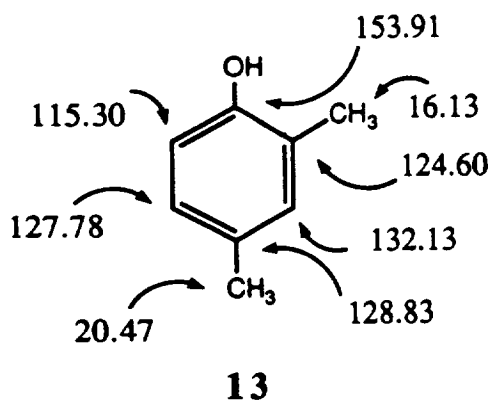
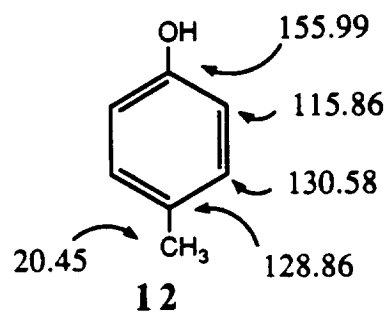
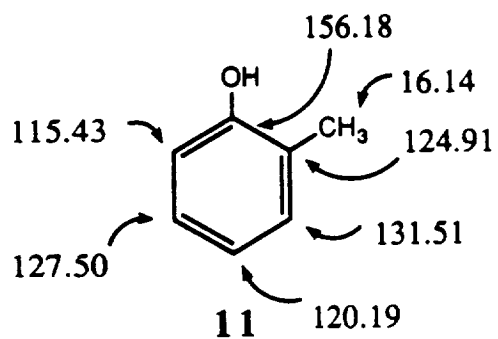
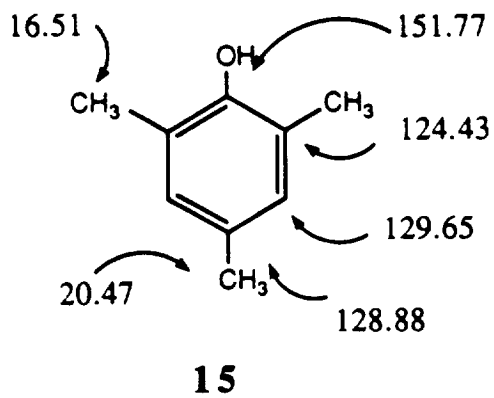
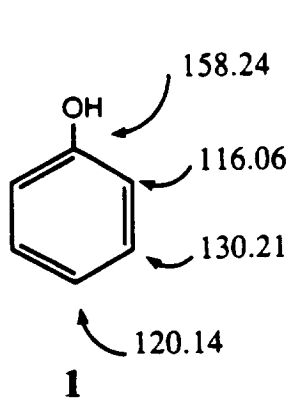
ASSIGNMENTS OF C-13 NMR OF PF MODEL COMPOUNDS, p 2

<u>C#</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>
1	155.99	153.91	154.07	151.77	-	152.41
2	115.86	124.60	124.60	124.43	-	127.57
3	130.58	132.13	129.14	129.65	-	127.61
4	128.86	128.83	120.27	128.88	-	128.54
5	130.58	127.78	129.14	129.65	-	127.61
6	115.86	115.30	124.60	124.43	-	127.57
o-R	-	16.13	16.54	16.51	-	62.26
m-R	-	-	-	-	-	-
p-R	20.45	20.47	-	20.47	-	20.60
Other	-	-	-	-	75.42 (all CH ₂) -	

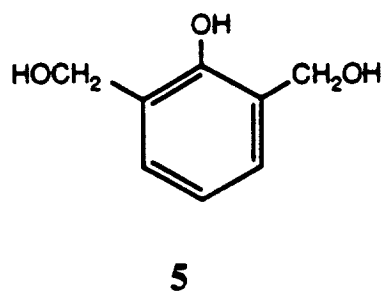
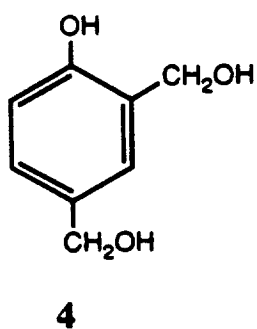
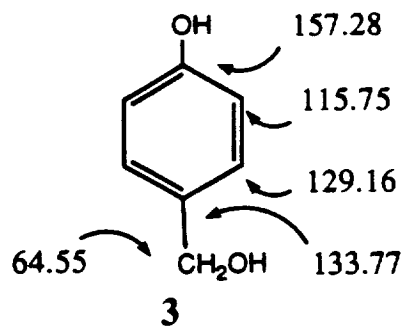
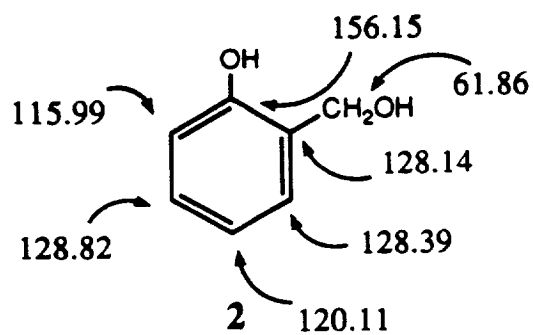
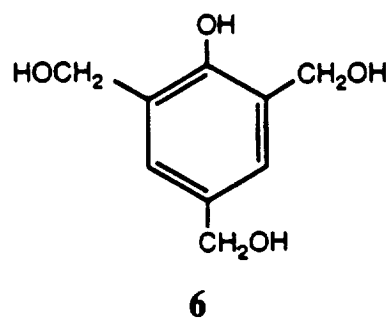
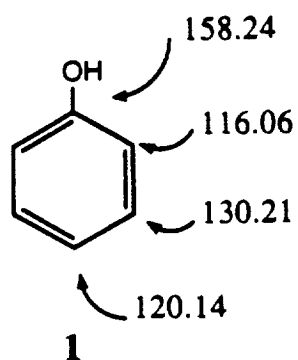
<u>C#</u>	<u>18</u>	<u>19</u>
1	158.22	
2	114.24	
3	144.89	
4	118.38	
5	129.94	
6	114.52	
o-R	-	
m-R	64.58	
p-R	-	
Other	-	

* present in PF resin

Assignments of C-13 Peaks of Methylphenols

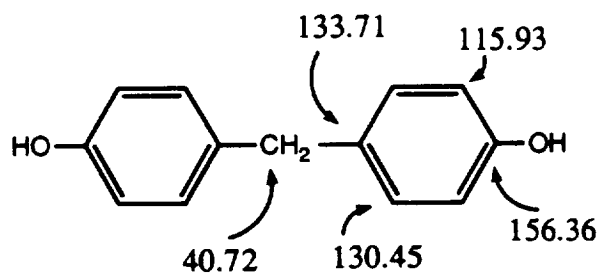
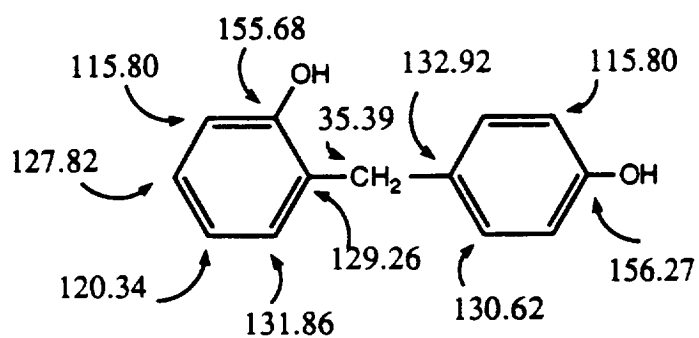
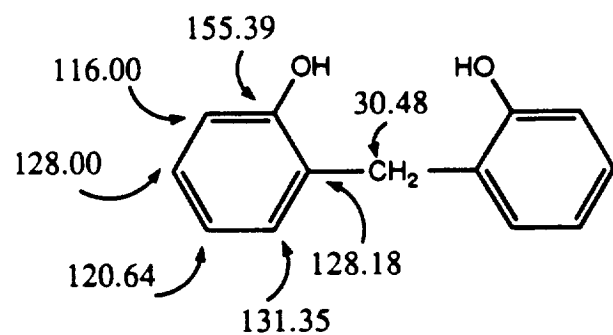


Assignments of C-13 Peaks of Methylolphenols

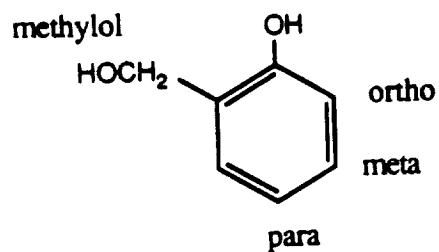


	-CH ₂ OH	C ₁	C ₂	C ₃	C ₄
A _i for methylol substituent	+12	-2	0	-1	

Assignments of C-13 Peaks for Diphenylmethanes



COMPOUND DISTRIBUTION IN RESIN



PHENOLICS

C-O Region
m-C and *o*- and *p*-C-R
p-C-H
o-C-H

FORMALDEHYDE

Formal,	OCH ₂ O
Methylol,	Ar CH ₂ OH
Amine,	ArCH ₂ N
Diphenylmethane	ArCH ₂ Ar



GE NMR
QE-300

NASR.002
13SEP91

PHENOL RESIN (NASA)

OPERATOR: FISHER

ONE PULSE SEQUENCE

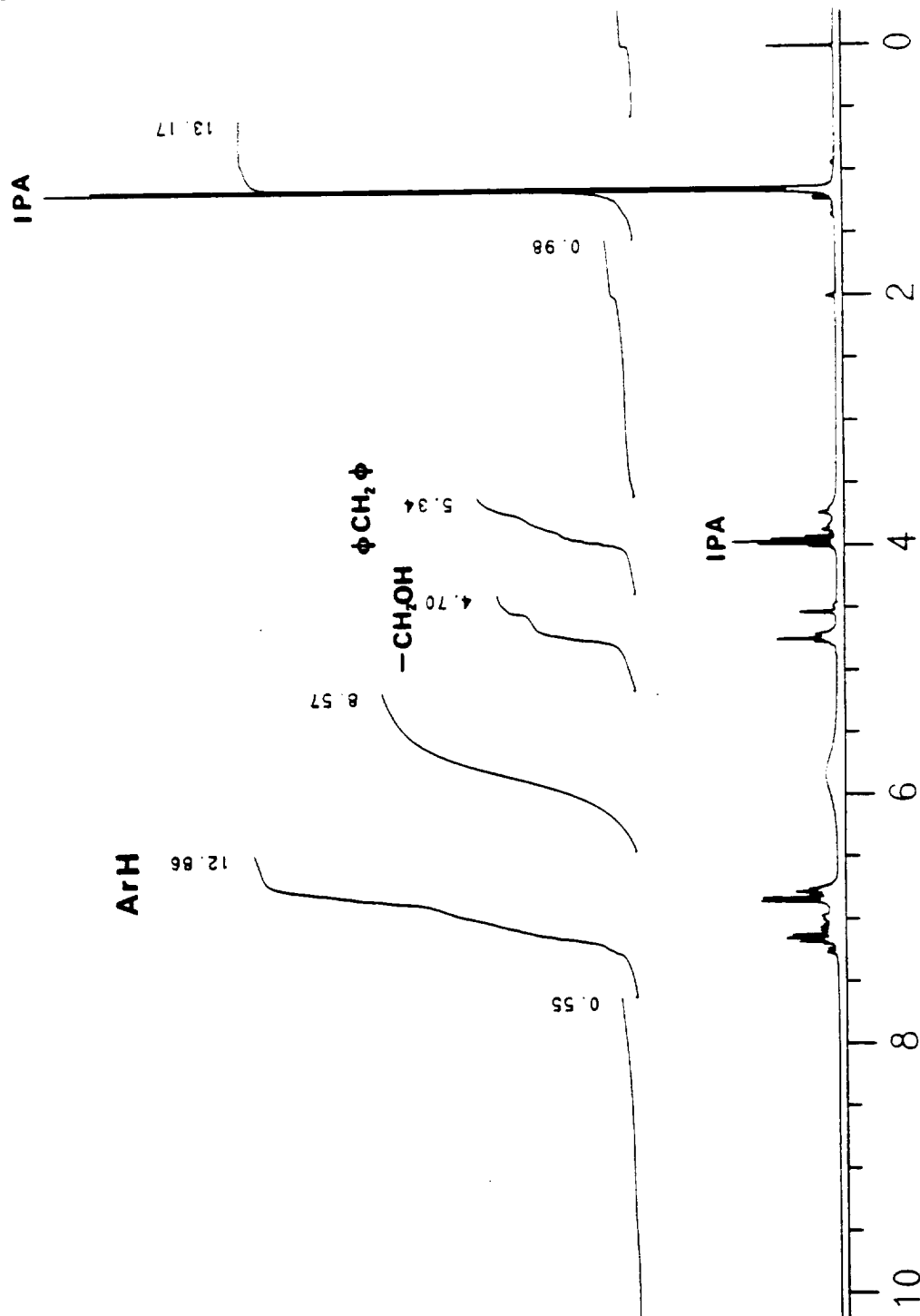
PULSE WIDTH = 3.33 USEC
ACQ. TIME = 29 DEGREES
RECYCLE TIME = 2.72 SEC
NO. OF ACQS = 3.71 SEC
DATA SIZE = 0
LINE BROADNG = 32768
SPIN RATE = .00 HZ
22 RPS

OBSERVE:
FREQUENCY = 300.668846 MHZ
SPEC WIDTH = 6024 HZ
GAIN = 37.1

HIGH POWER ON
HIGH POWER OUTPUT = 62 DB

PLOT SCALE:
157.86 HZ/CM
5250 PPM/CM
FROM 10.19
TO -29 PPM

H-1





GE NMR
QE-300

NASR.003
13SEP91

PHENOL RESIN (NASR)

OPERATOR FISHER

UNE PULSE SEQUENCE

PULSE WIDTH = 4.47 USEC
AQ TIME = 30 DEGR
RECYCLE TIME = 0.1920 SEC
NO OF ACQS = 482
DATA SIZE = 32768
LINE BROADENING = 1.00 HZ
SPIN RATE = 22 RPS

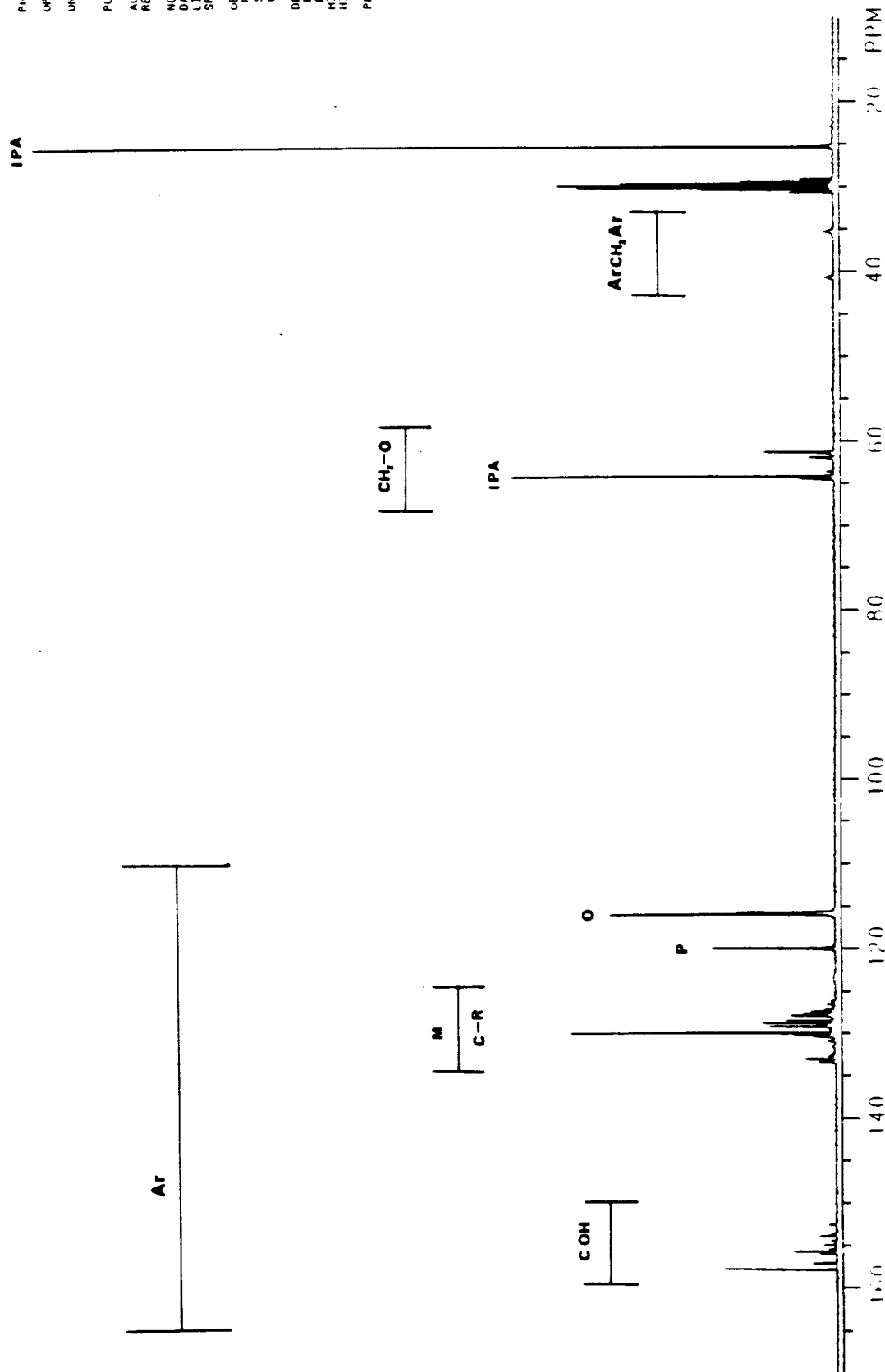
OBSERVE FREQUENCY = 75.610844 MHz
SPEC WIDTH = 20000 HZ
GAIN = 68.1

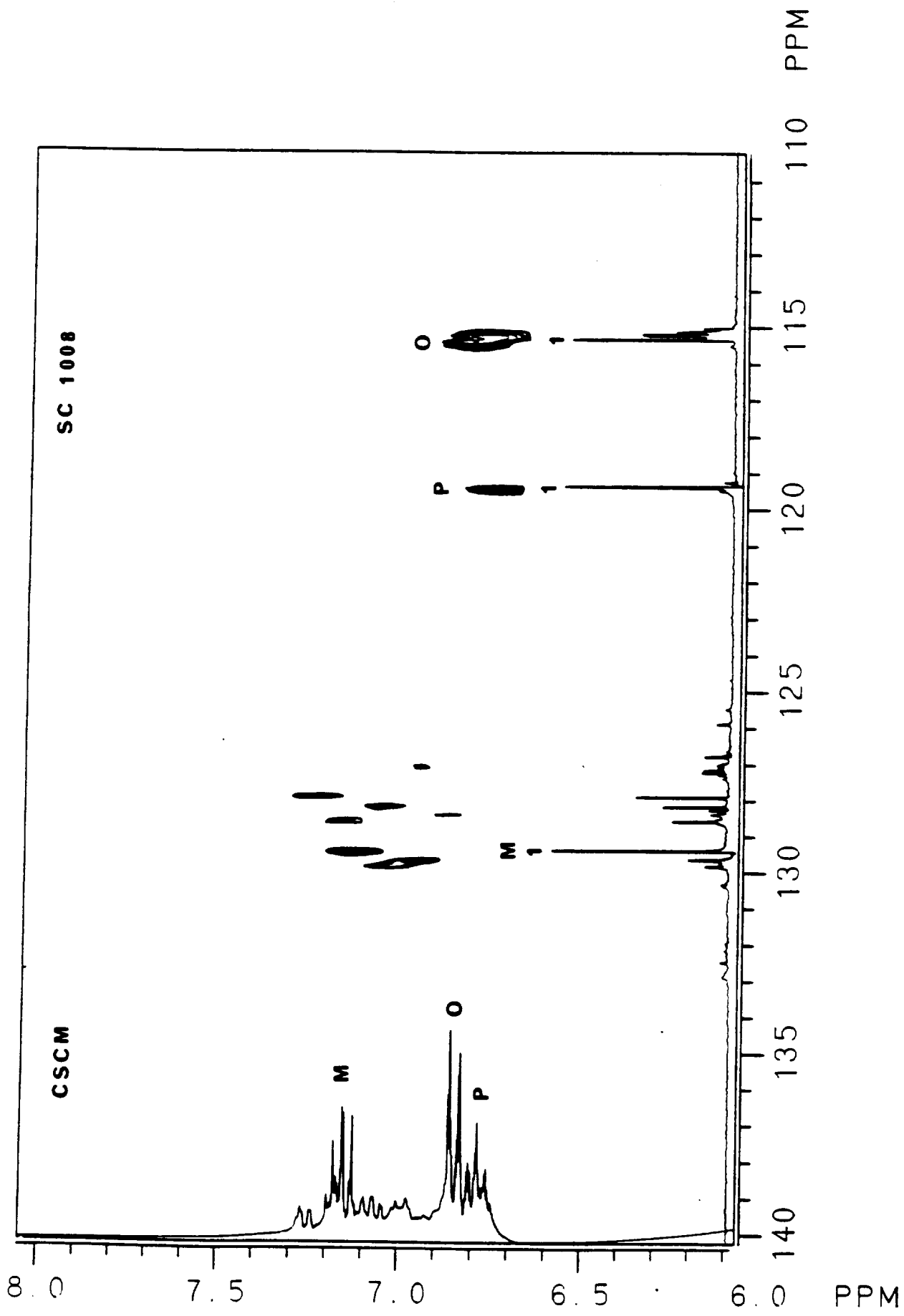
DECOUPLER STANDARD 64 MODULATED
FREQUENCY = 40000 PPM
POWER = 2000/3000
HIGH POWER ON
HIGH POWER OUTPUT = 61.70 W

PLOT SCALE

155.83 HZ/CM
FROM 170.00
TO 10.00 PPM

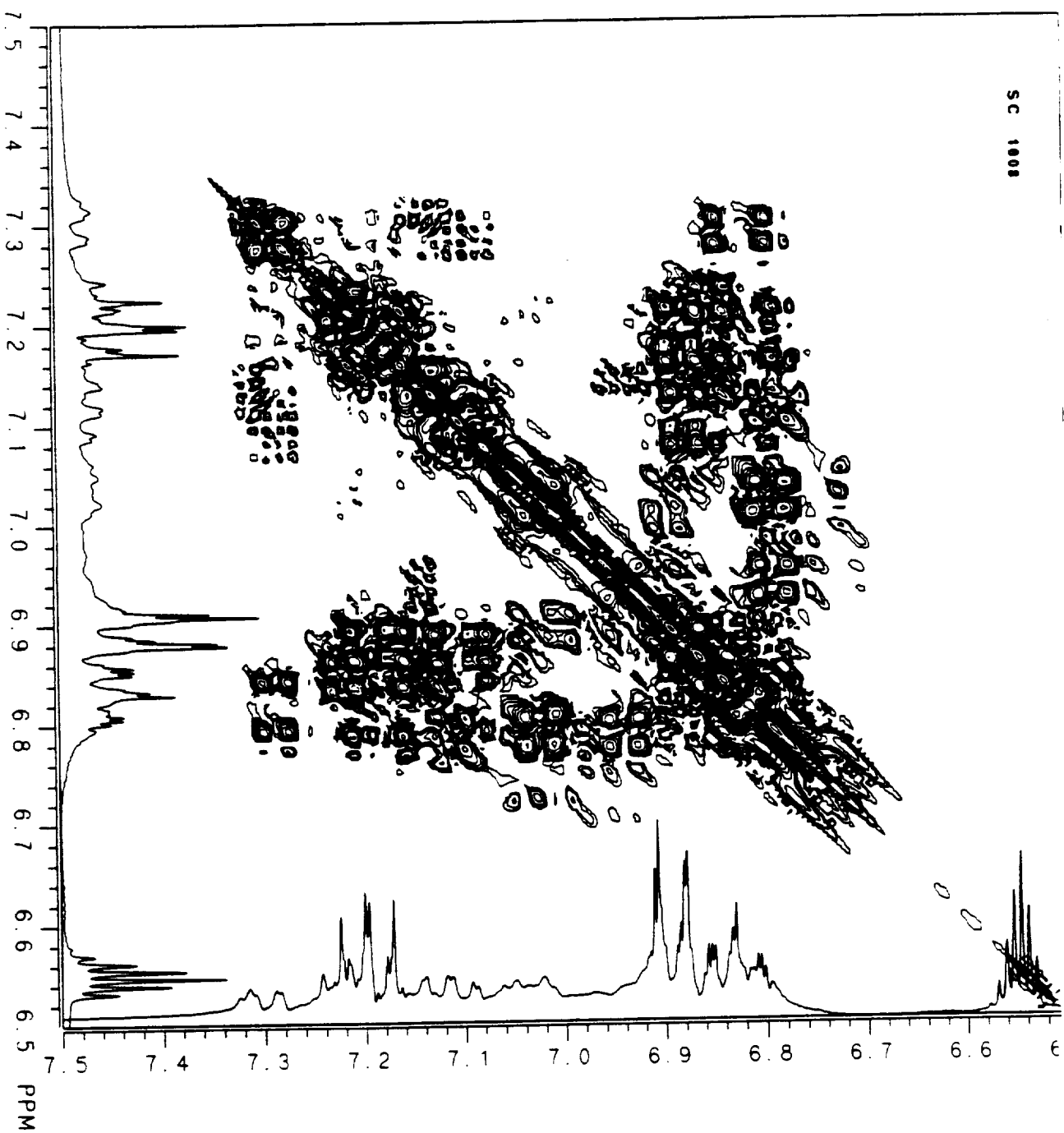
C-13

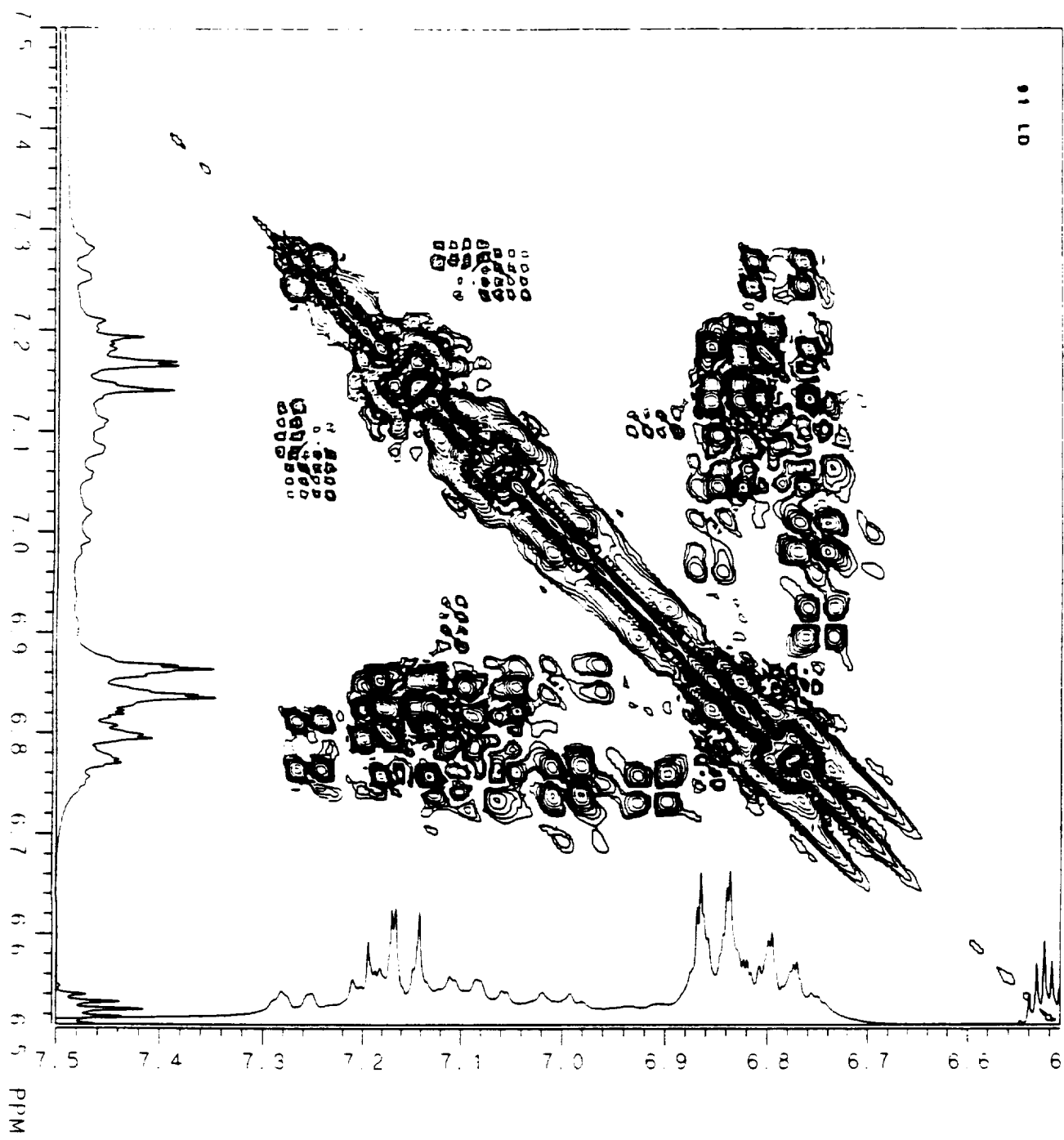




SC 1008

NMR
 $\gamma=3$
 $\lambda=$

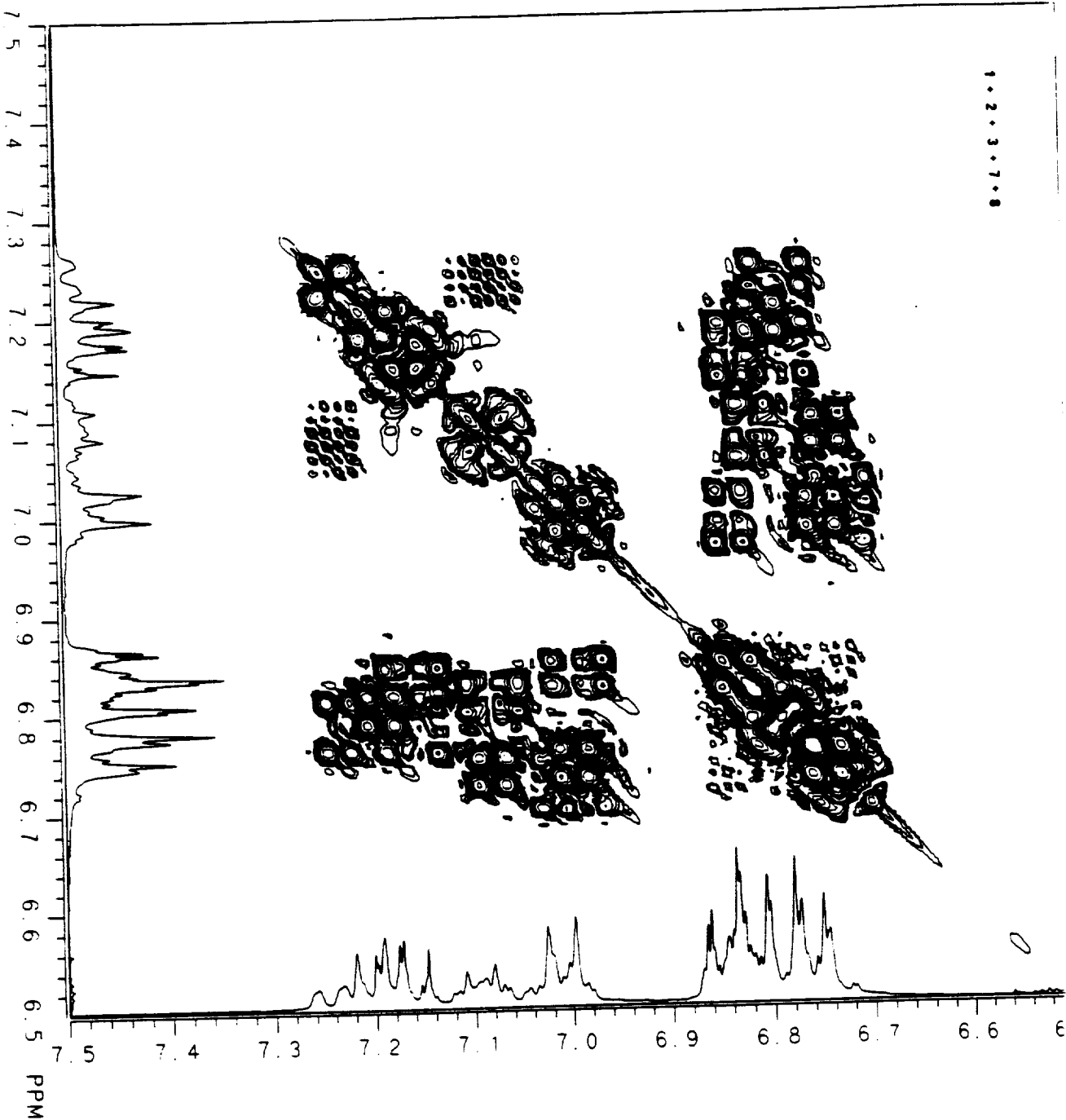


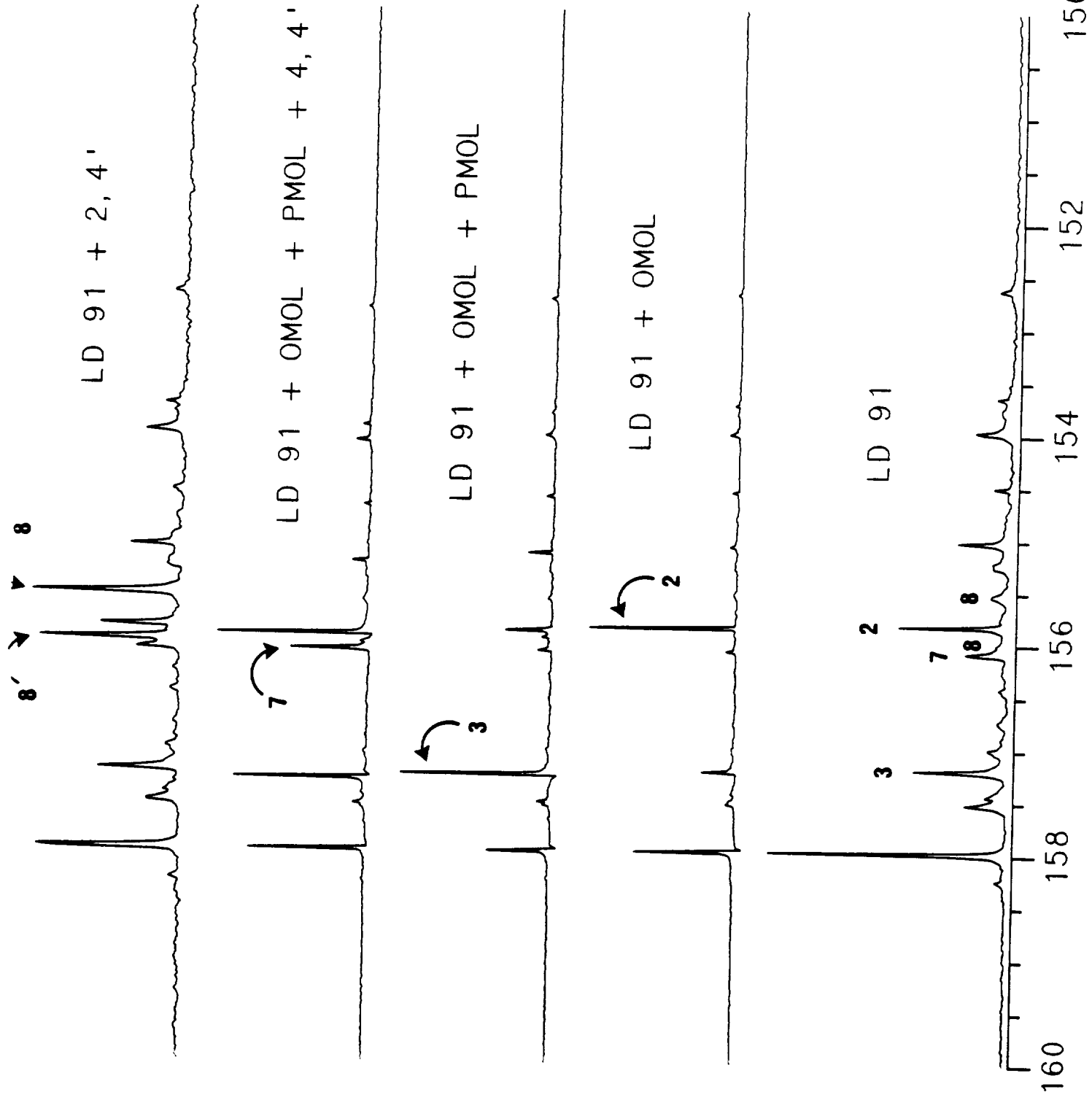


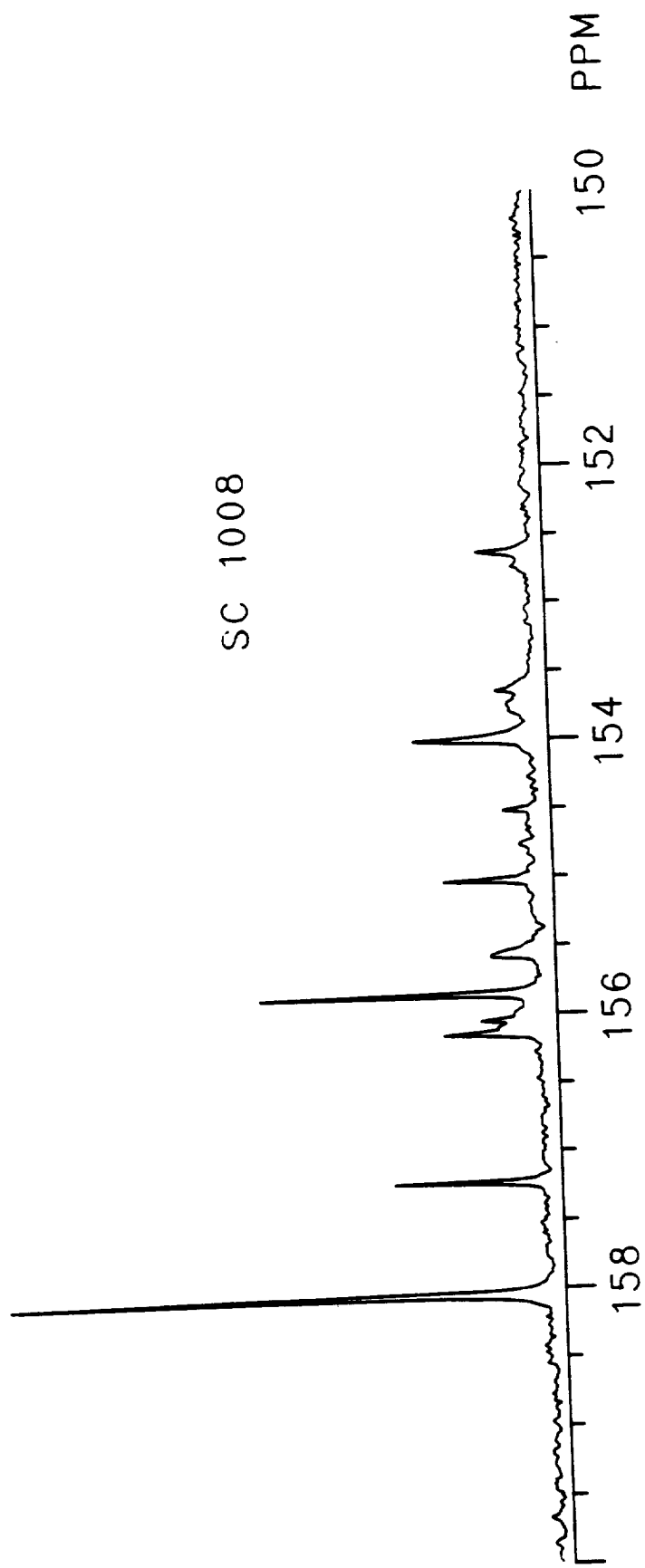
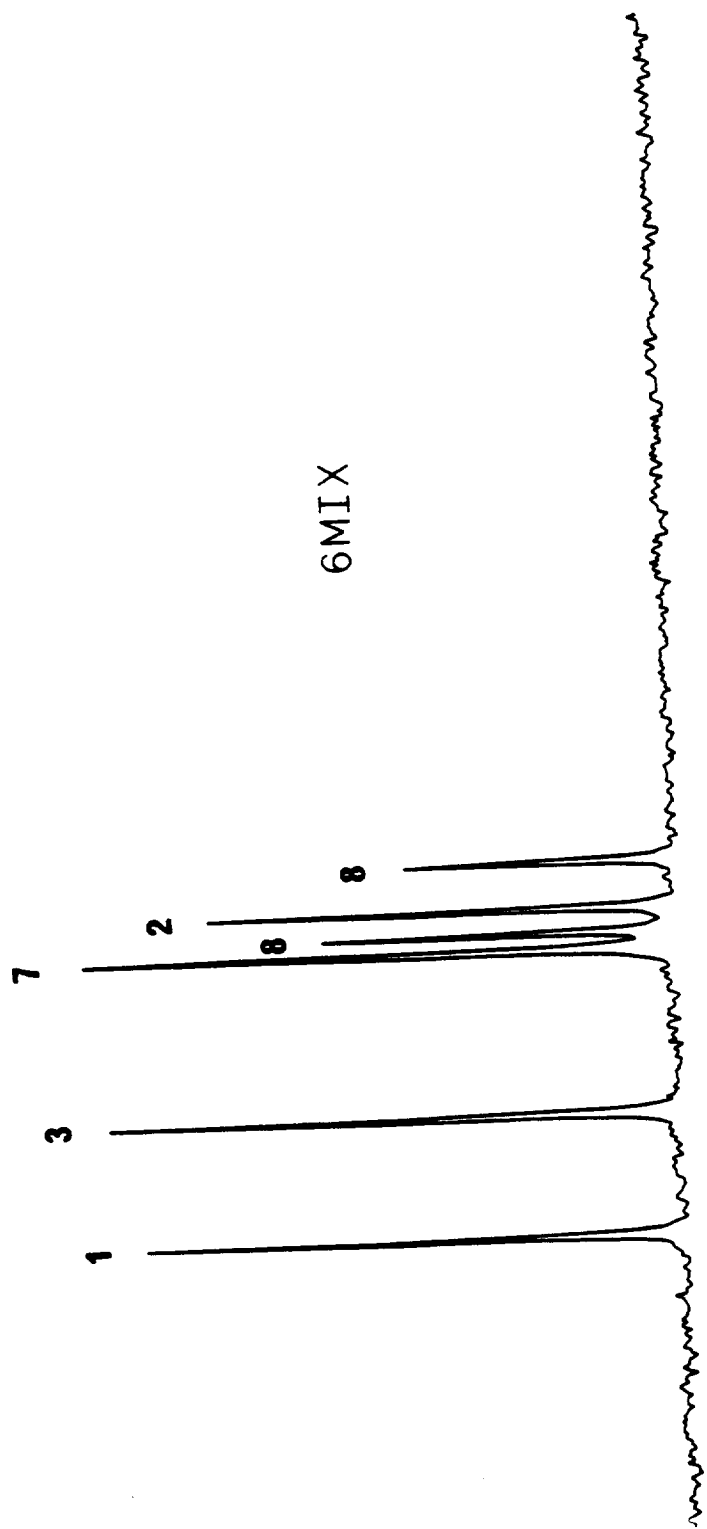
01 LD

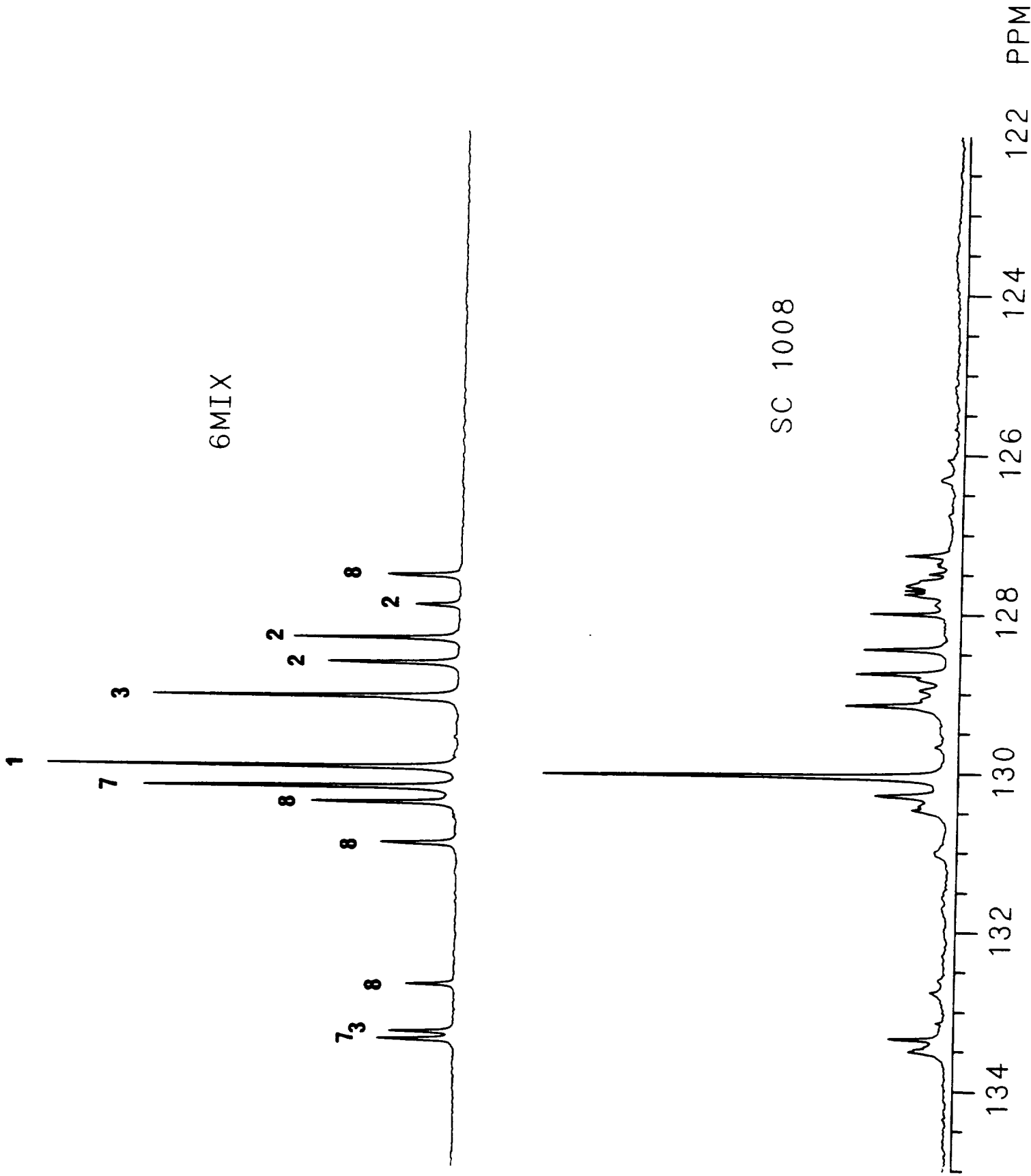
NALD21

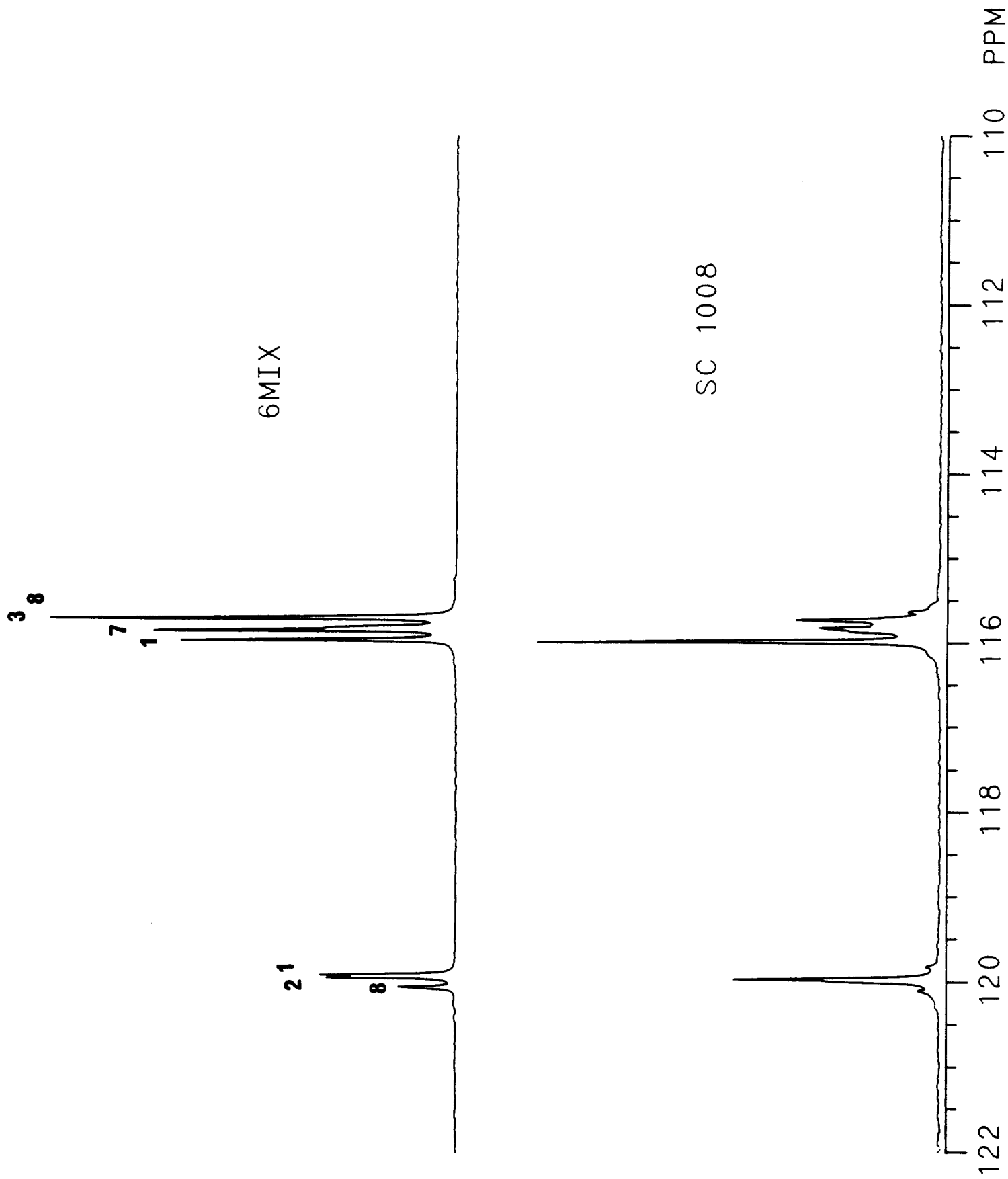
1.2.3.7.8











IPA

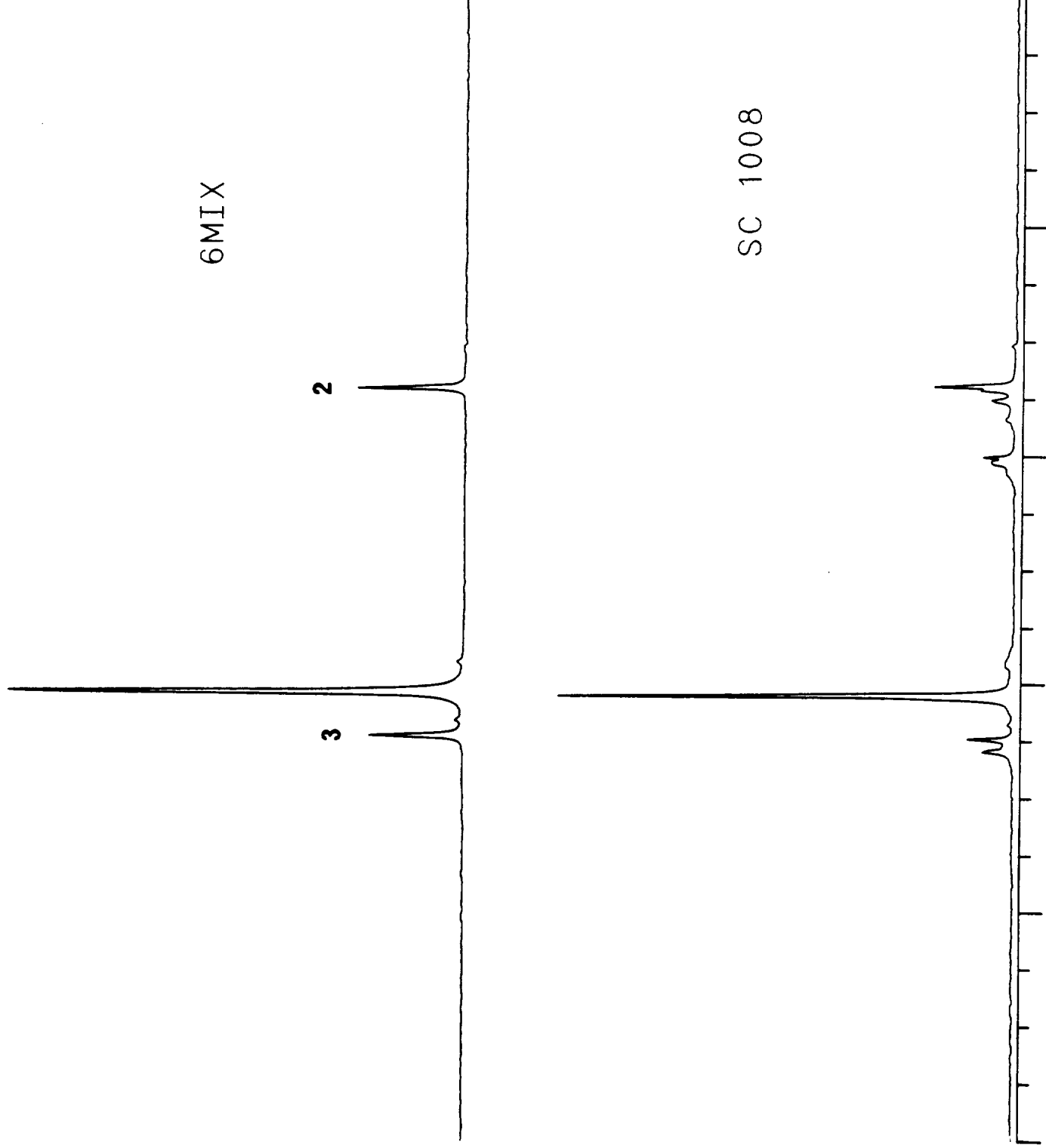
6MIX

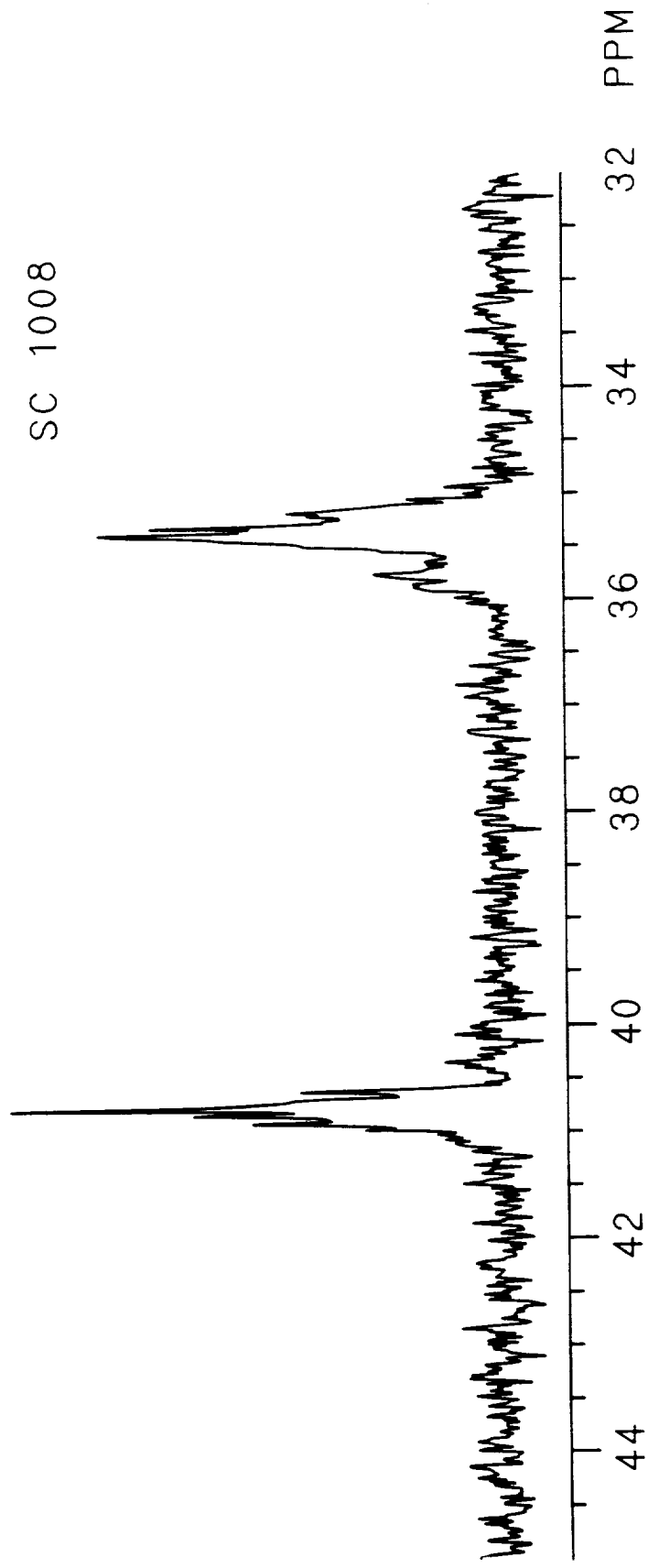
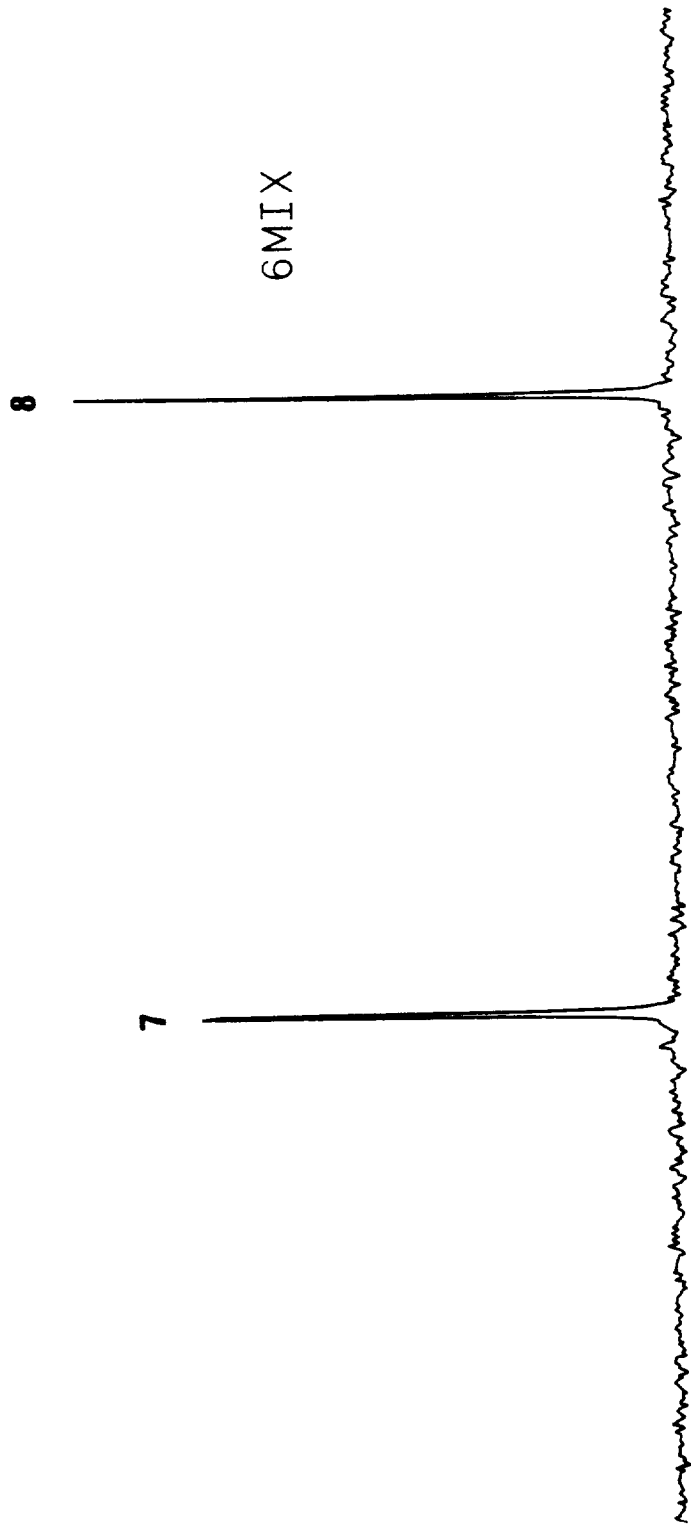
2

3

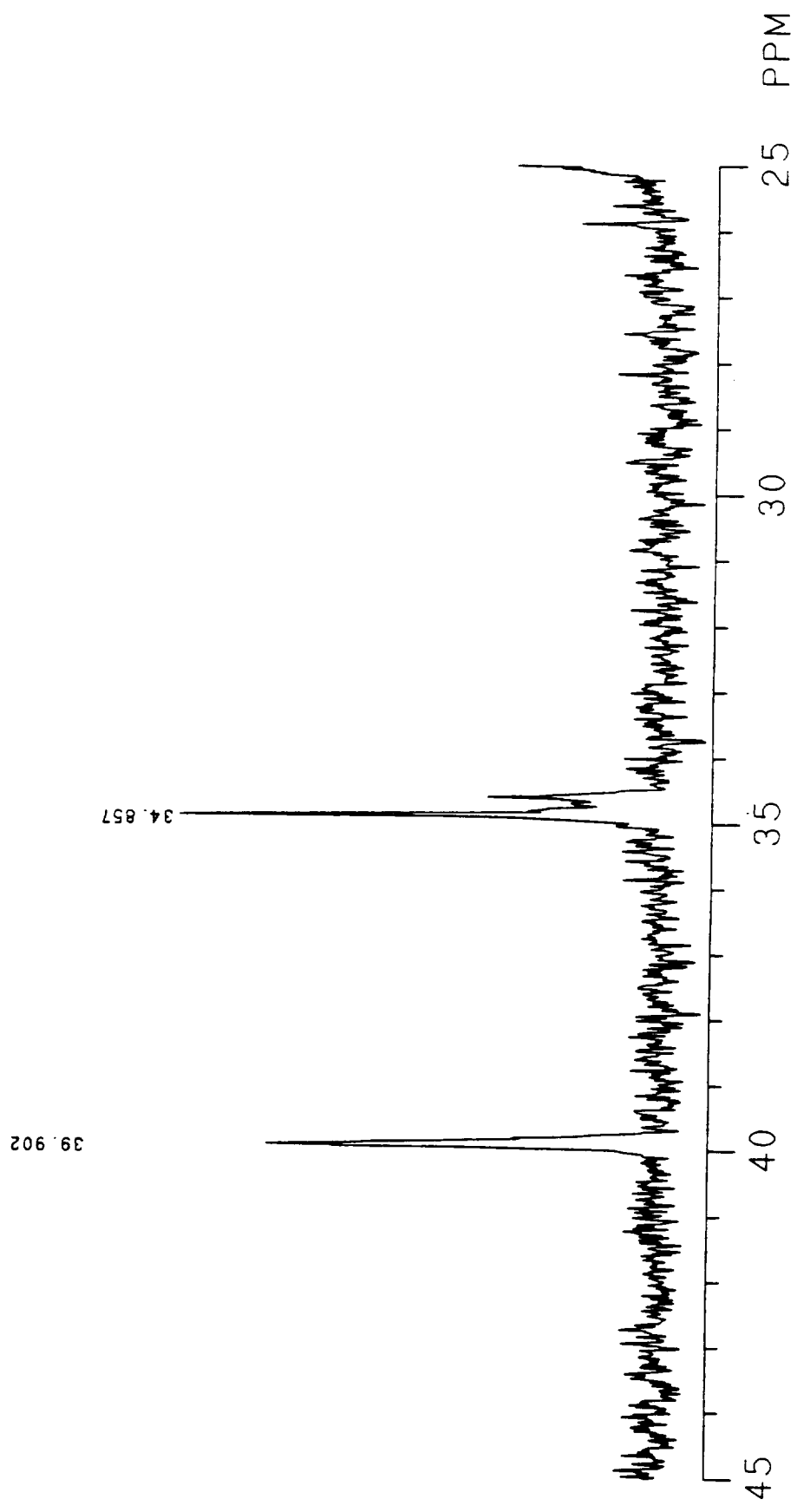
SC 1008

68 66 64 62 60 58 PPM





SC 1008 IN CDCl_3

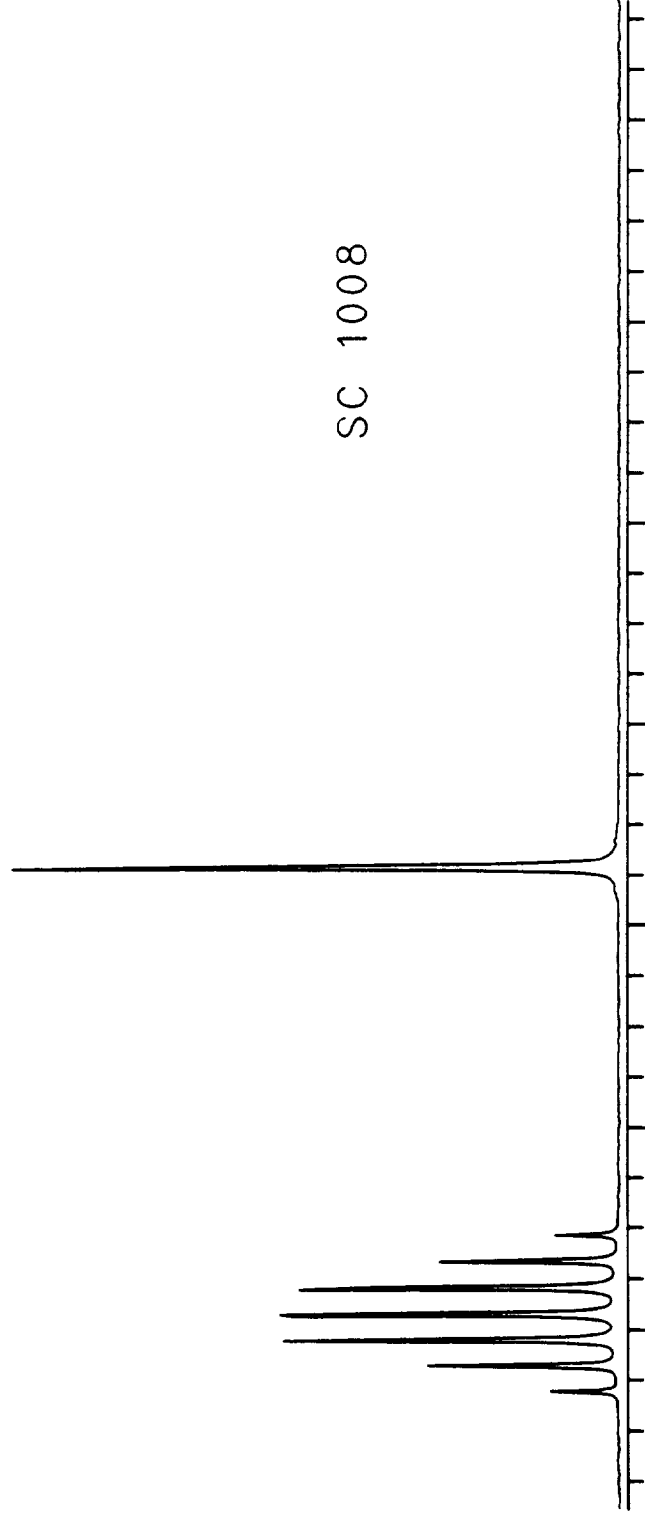
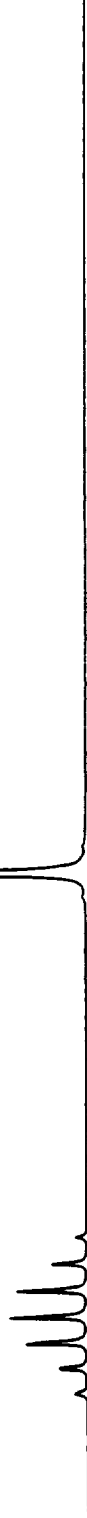


IPA

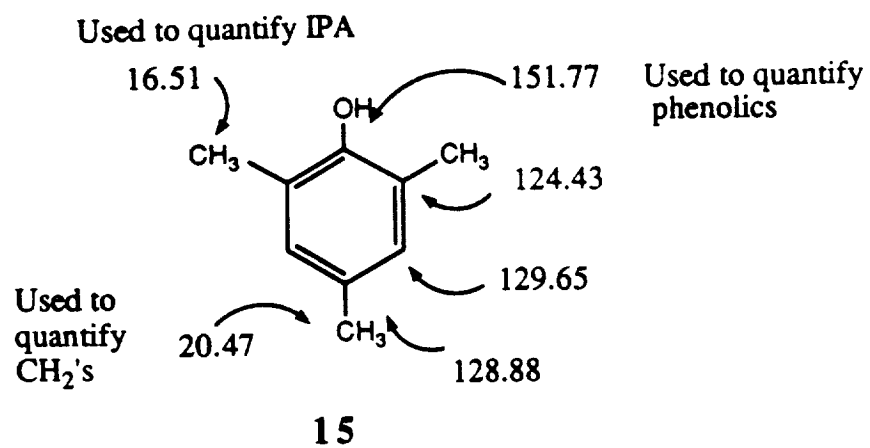
6MIX

SC 1008

30 28 26 24 22 20 18 PPM

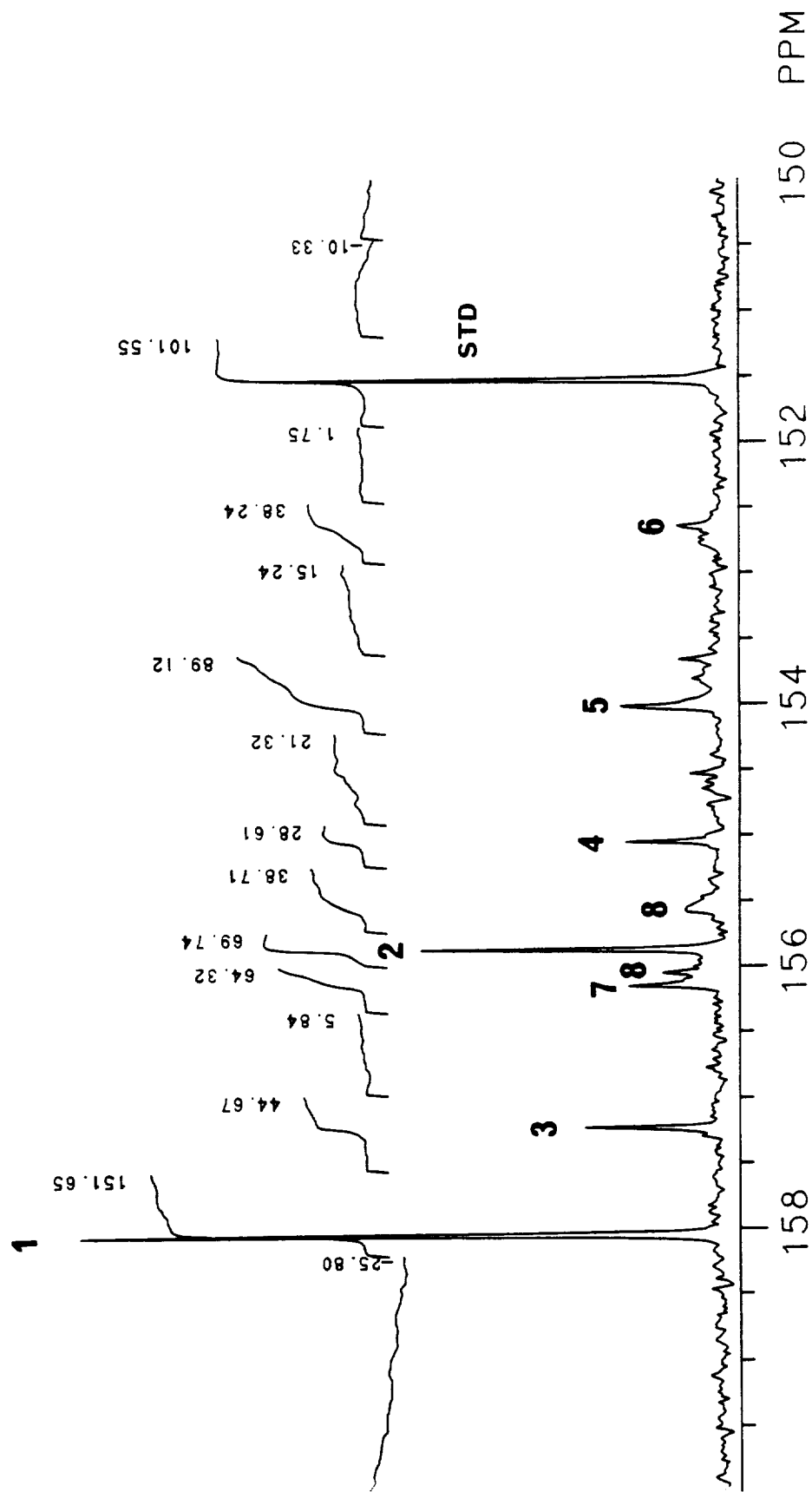


INTERNAL STANDARD



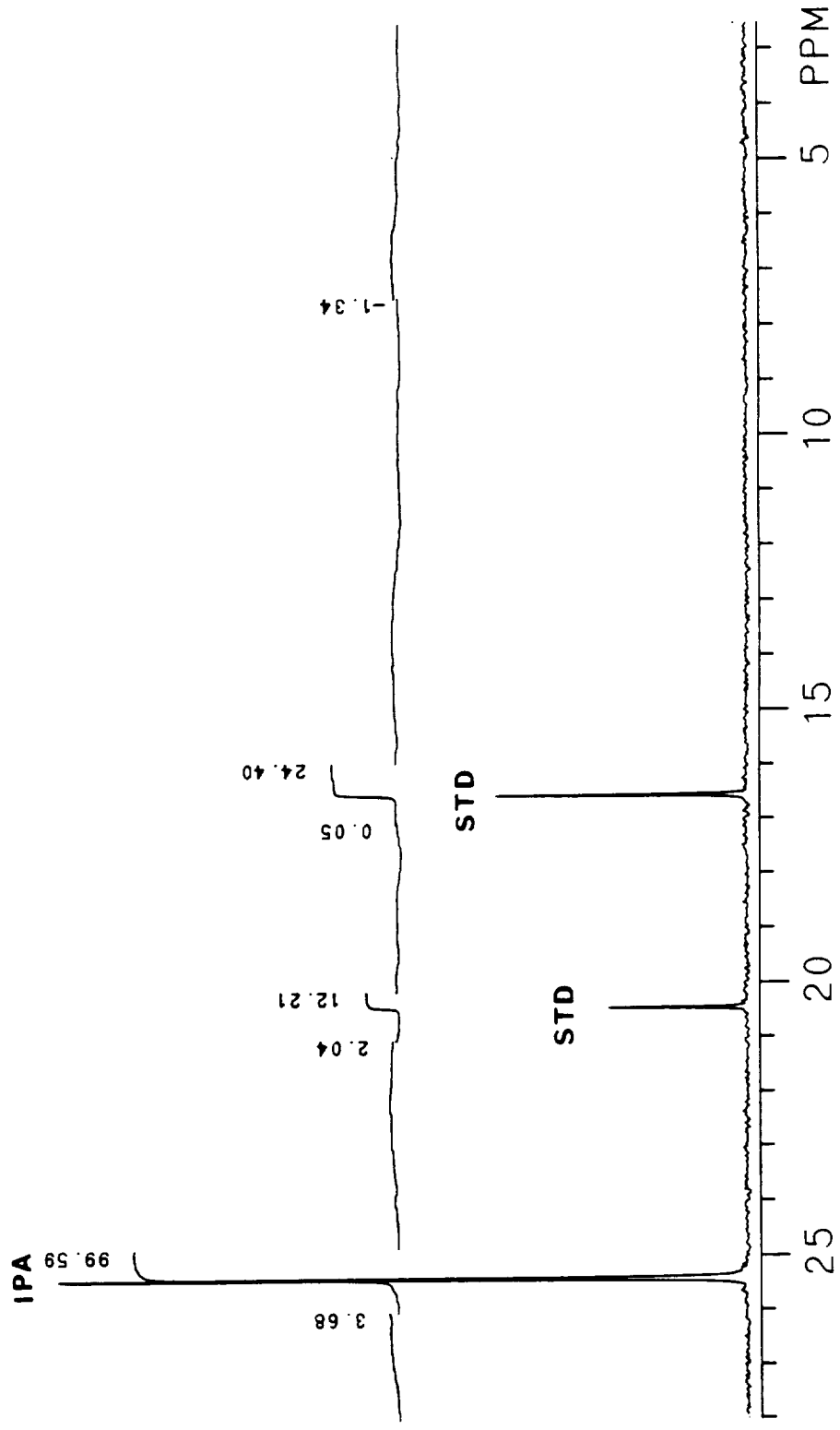
2,4,6-Trimethylphenol

SC 1008



STD

SC 1008



AMOUNTS OF COMPOUNDS 1 TO 8 IN PF RESIN

<u>COMPOUND</u>	<u>SC 1008 (wt. %)</u>	<u>91 LD (wt. %)</u>
1	12.9	15.0
2	7.9	10.9
3	5.0	9.3
4	4.0	3.4
5	7.3	8.1
6	6.4	3.3
7	2.3	3.4
8	7.0	6.5
IPA	<u>22.5</u>	<u>13.6</u>
Total:	75.3 wt. %	73.5 wt. %

Phenolics unassigned: 14.3 (mole %)

25.7 (mole %)

AMOUNTS OF COMPOUNDS 1 TO 8 IN PF RESIN

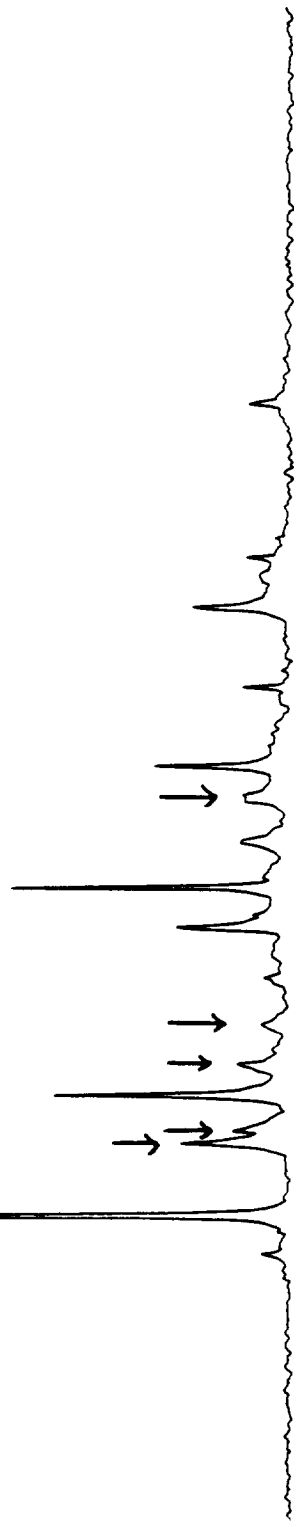
COMPOUND	SC 1008 (wt. %)	91 LD (wt. %)	SC 1008 (wt. %) PREPREG
1	12.9	15.0	13.1
2	7.9	10.9	8.8
3	5.0	9.3	4.4
4	4.0	3.4	5.2
5	7.3	8.1	9.3
6	6.4	3.3	4.9
7	2.3	3.4	3.4
8	7.0	6.5	6.1
IPA	22.5	13.6	26.0
Total:	75.3 wt. %	73.5 wt. %	81.2 wt. %

Phenolics unassigned: 14.3 (mole %)

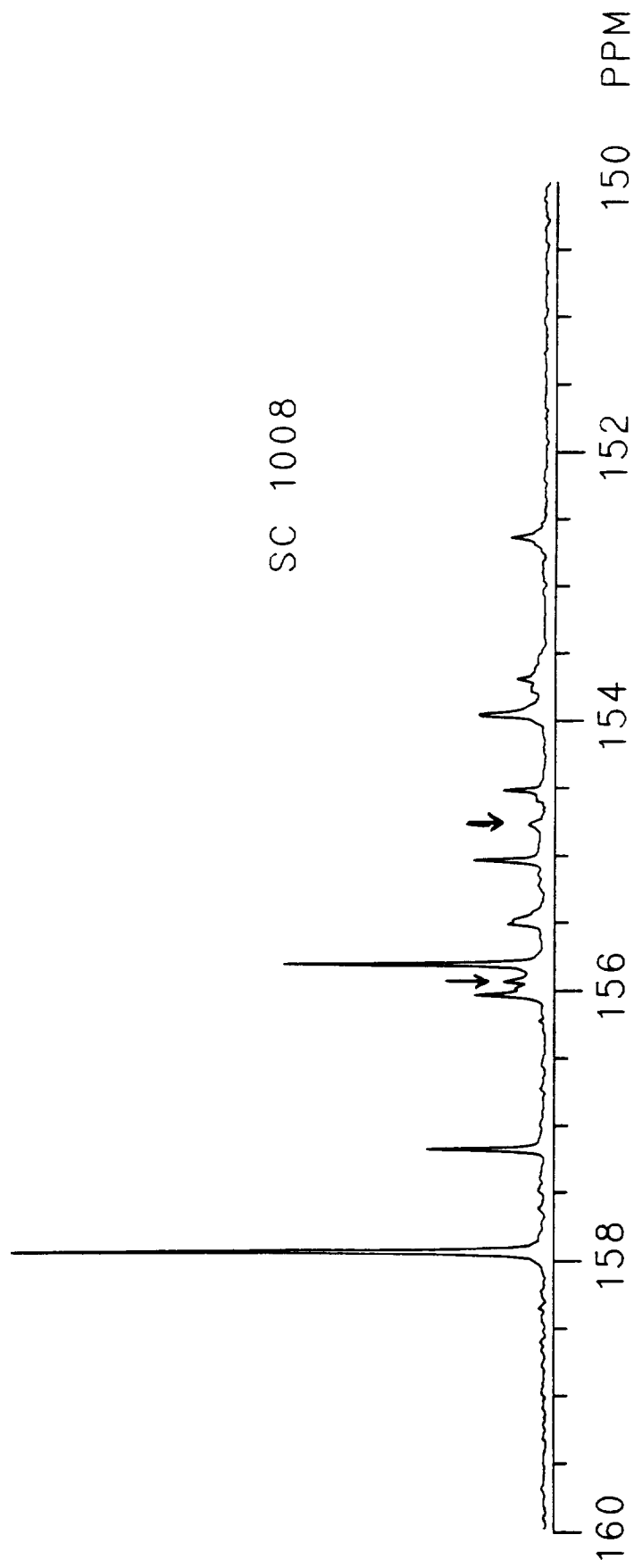
25.7 (mole %) 16.3 (mole %)



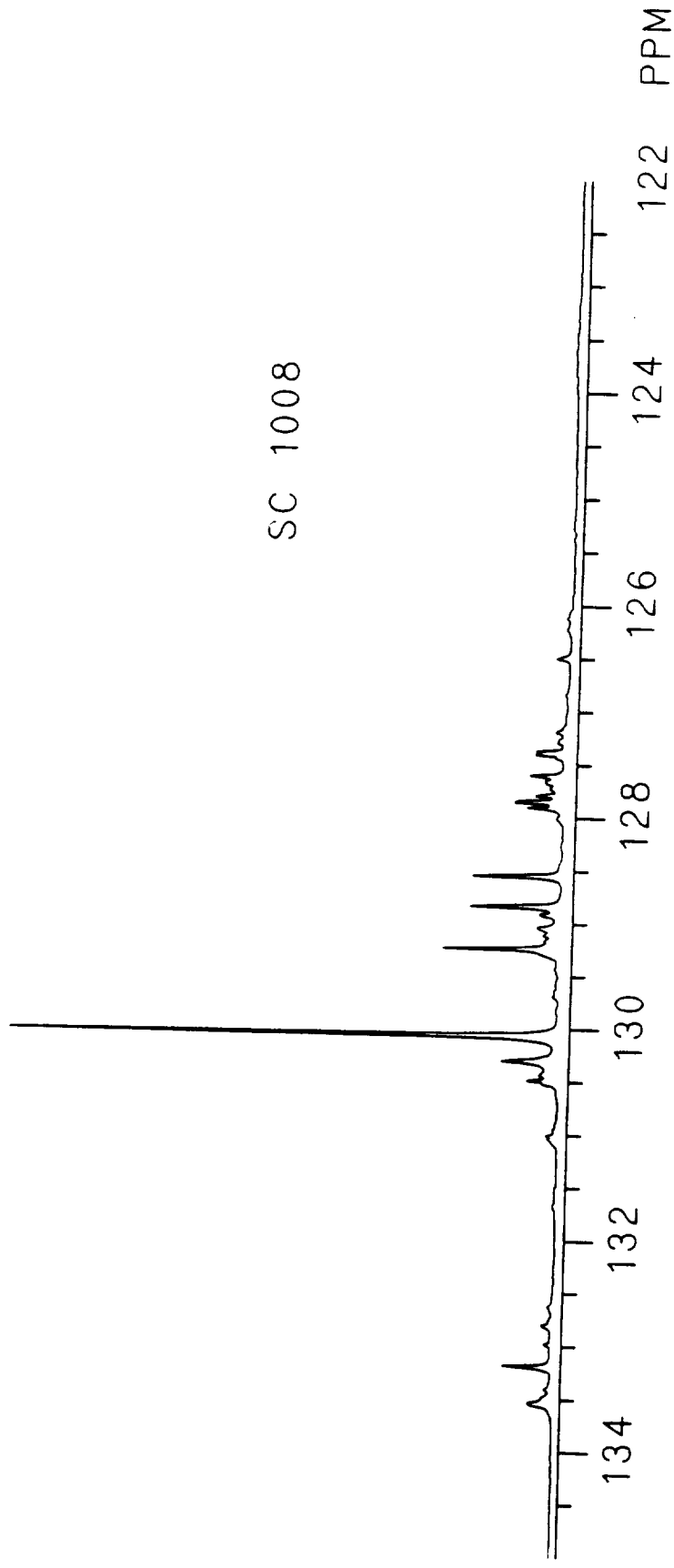
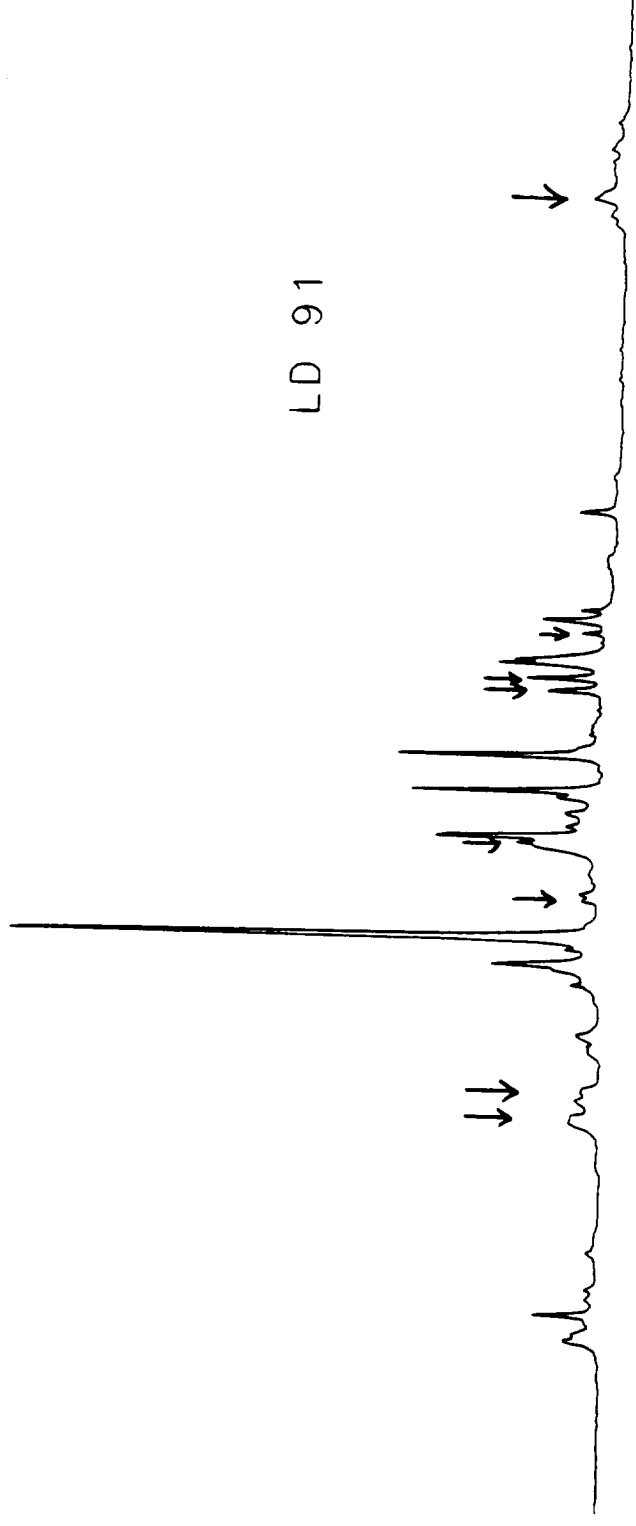
LD 91

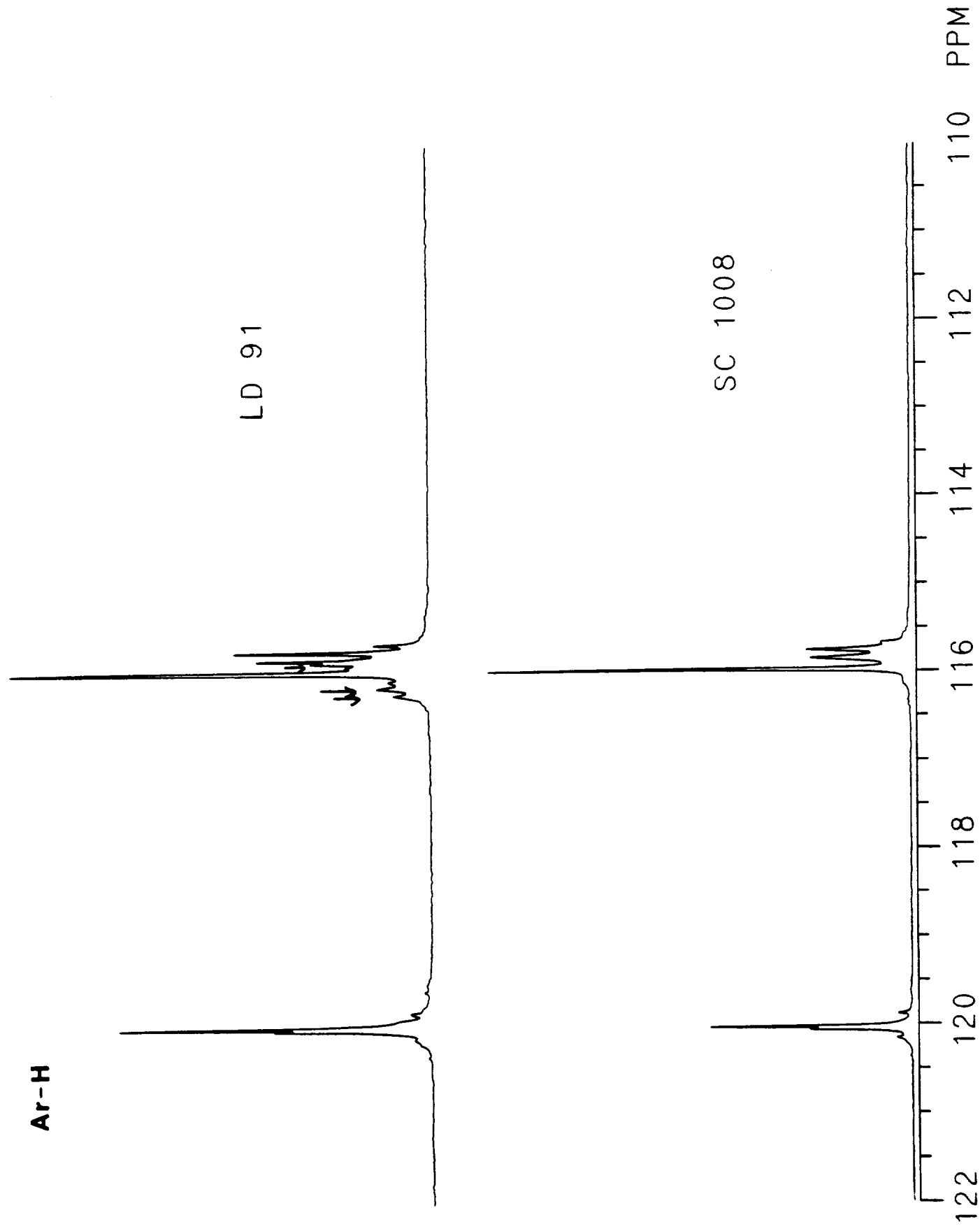


SC 1008



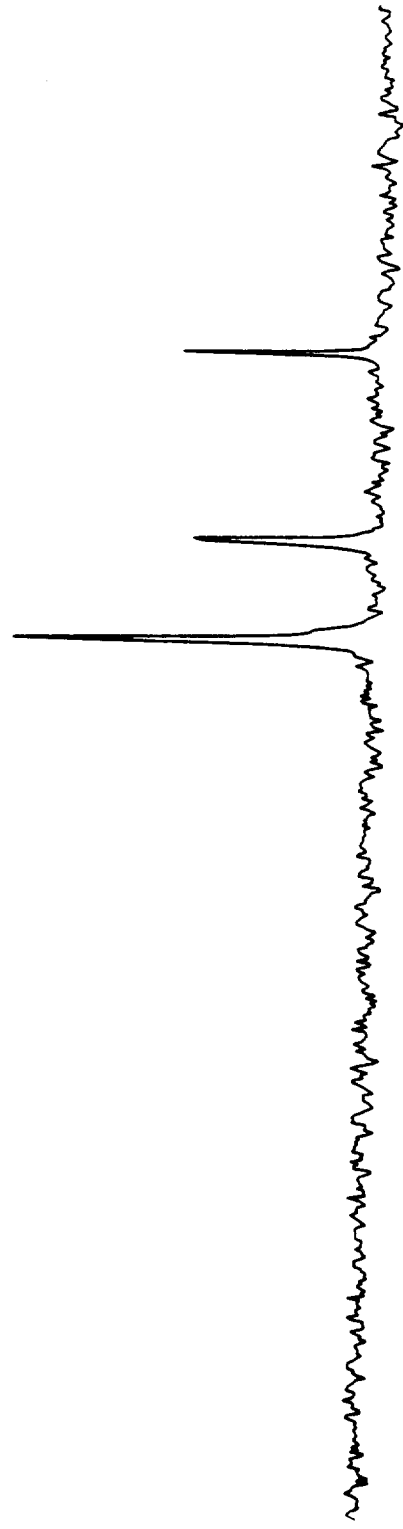
Ar



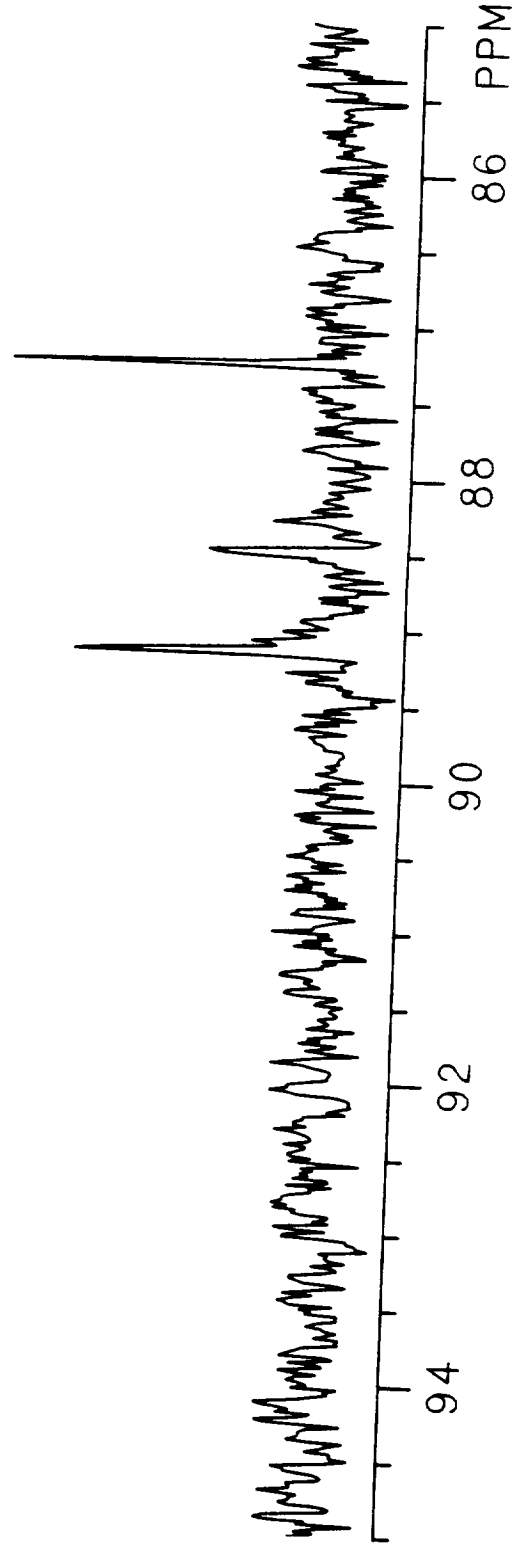


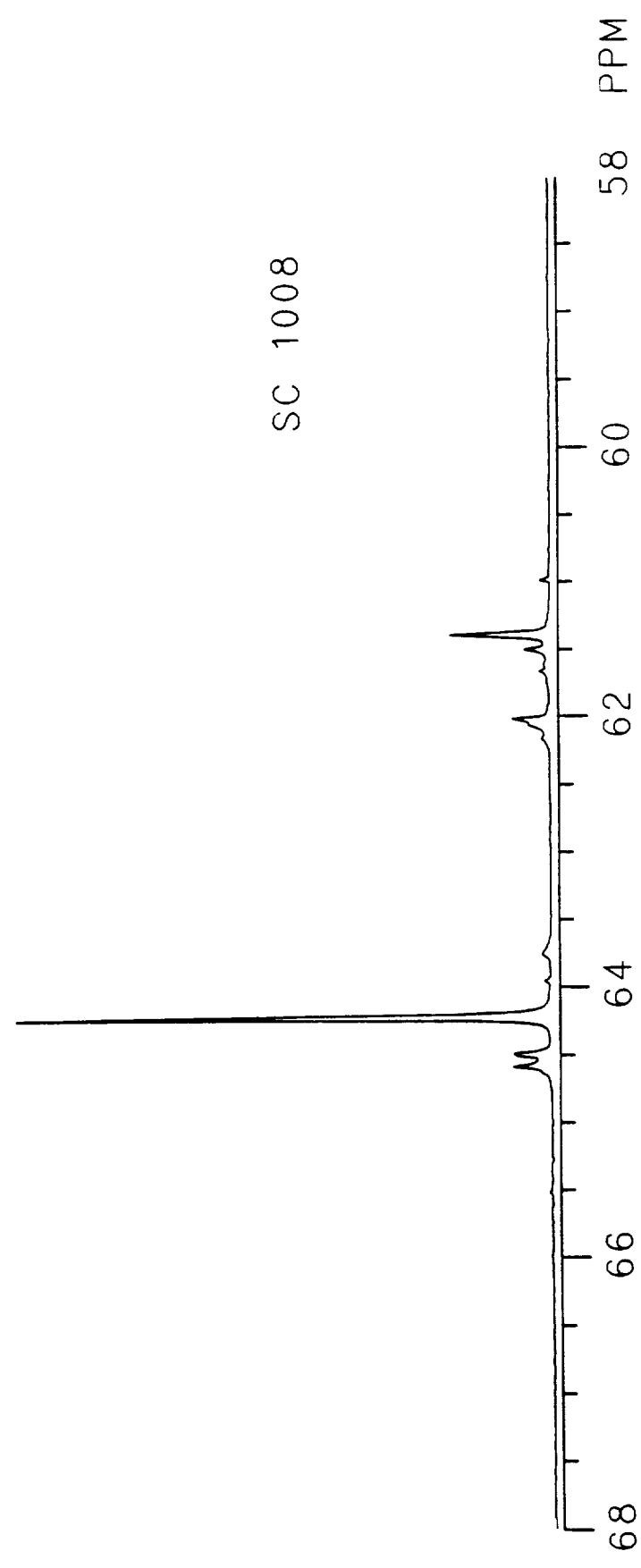
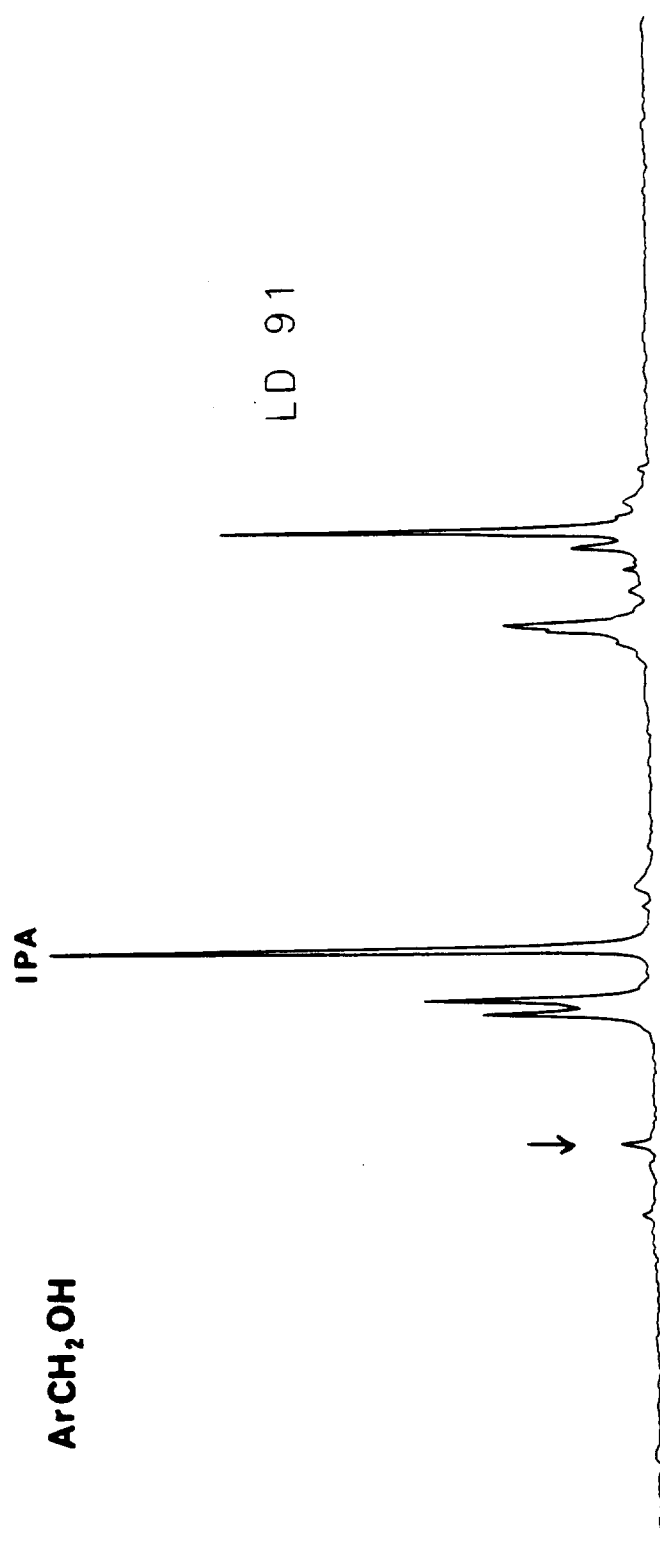
O CH₂O

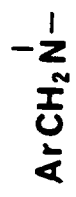
91 LD



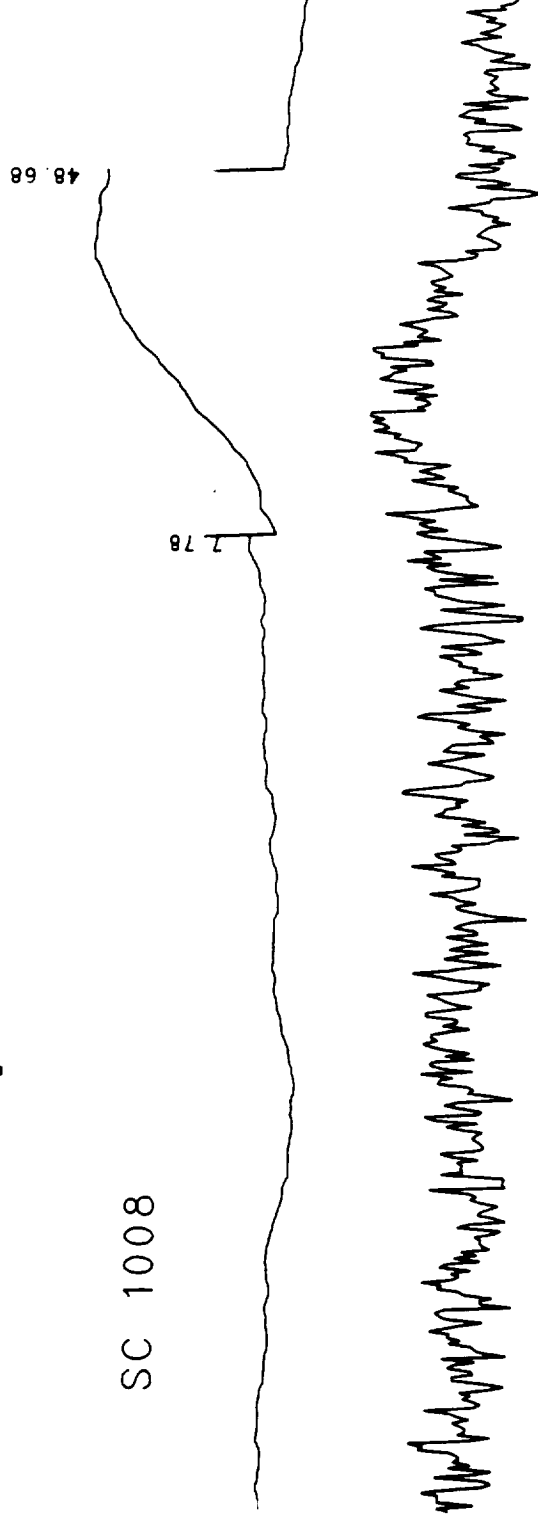
SC 1008



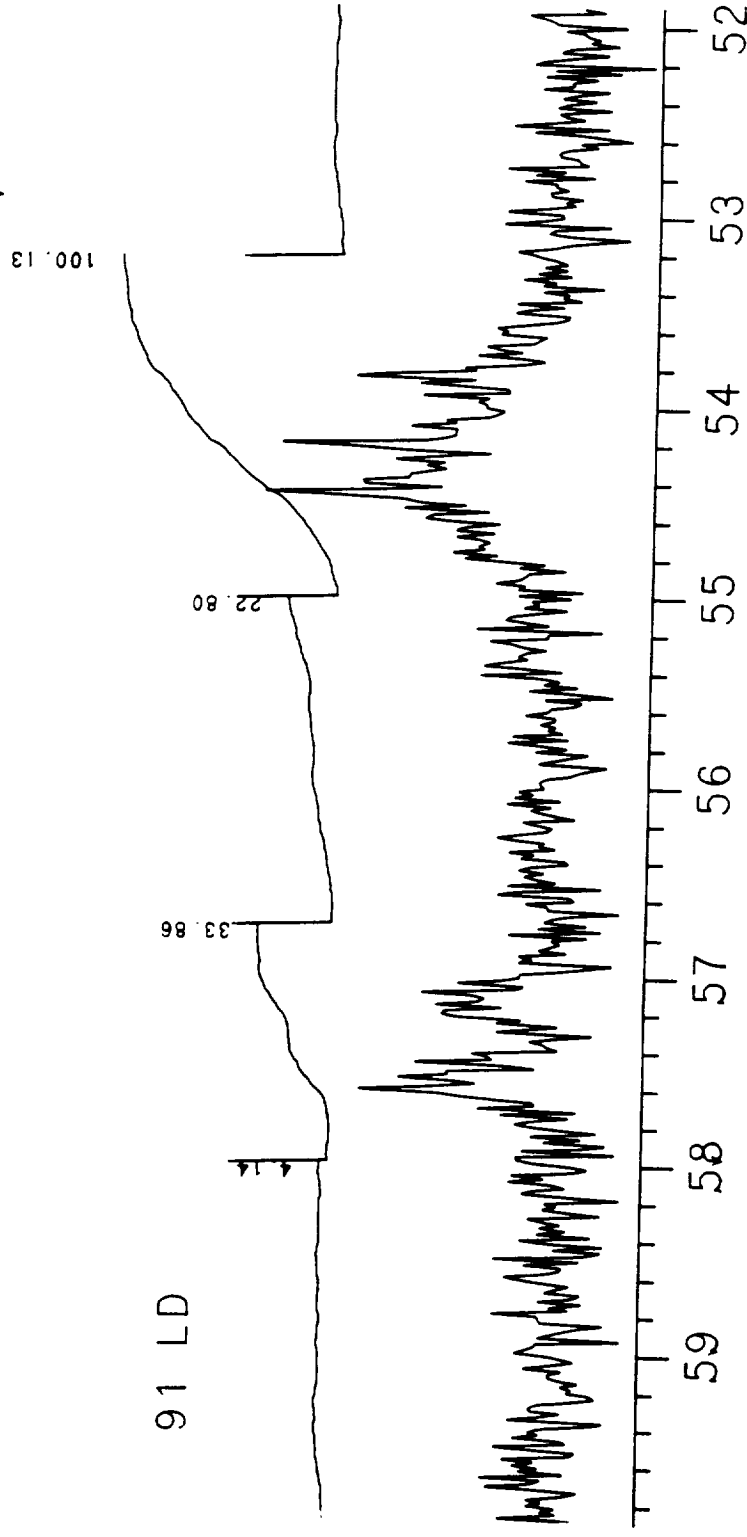




SC 1008

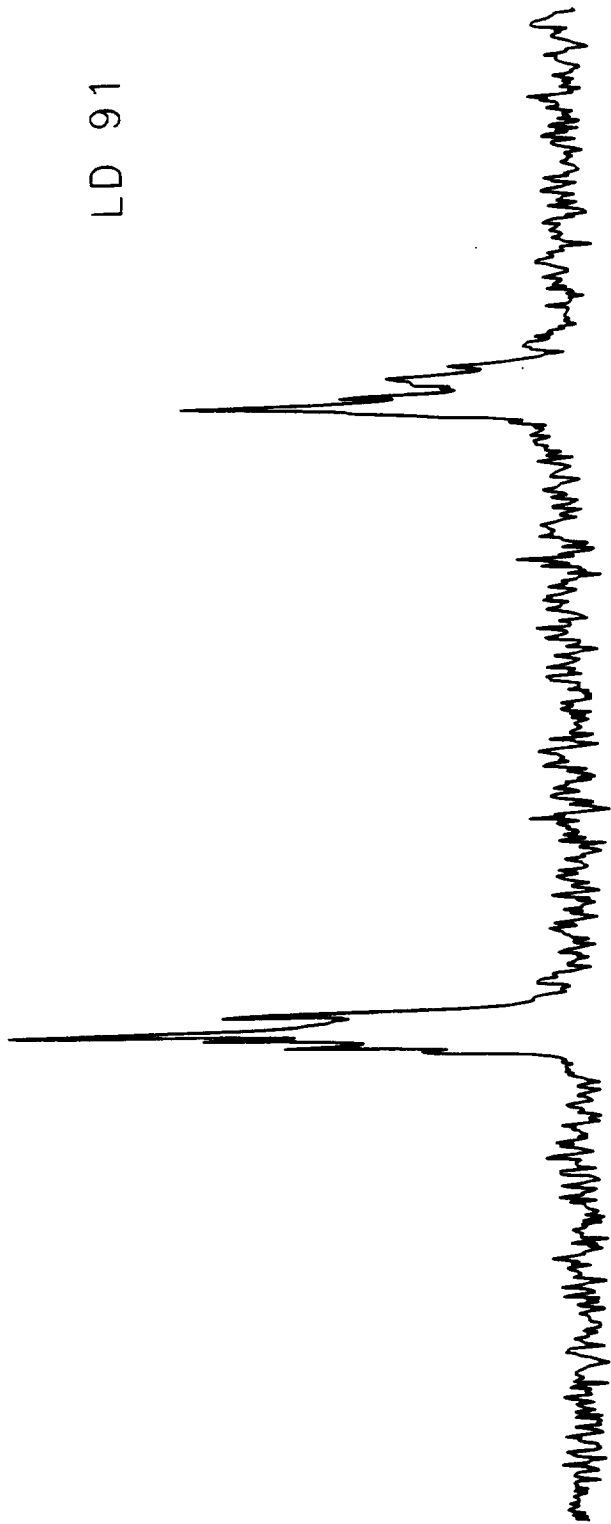


91 LD

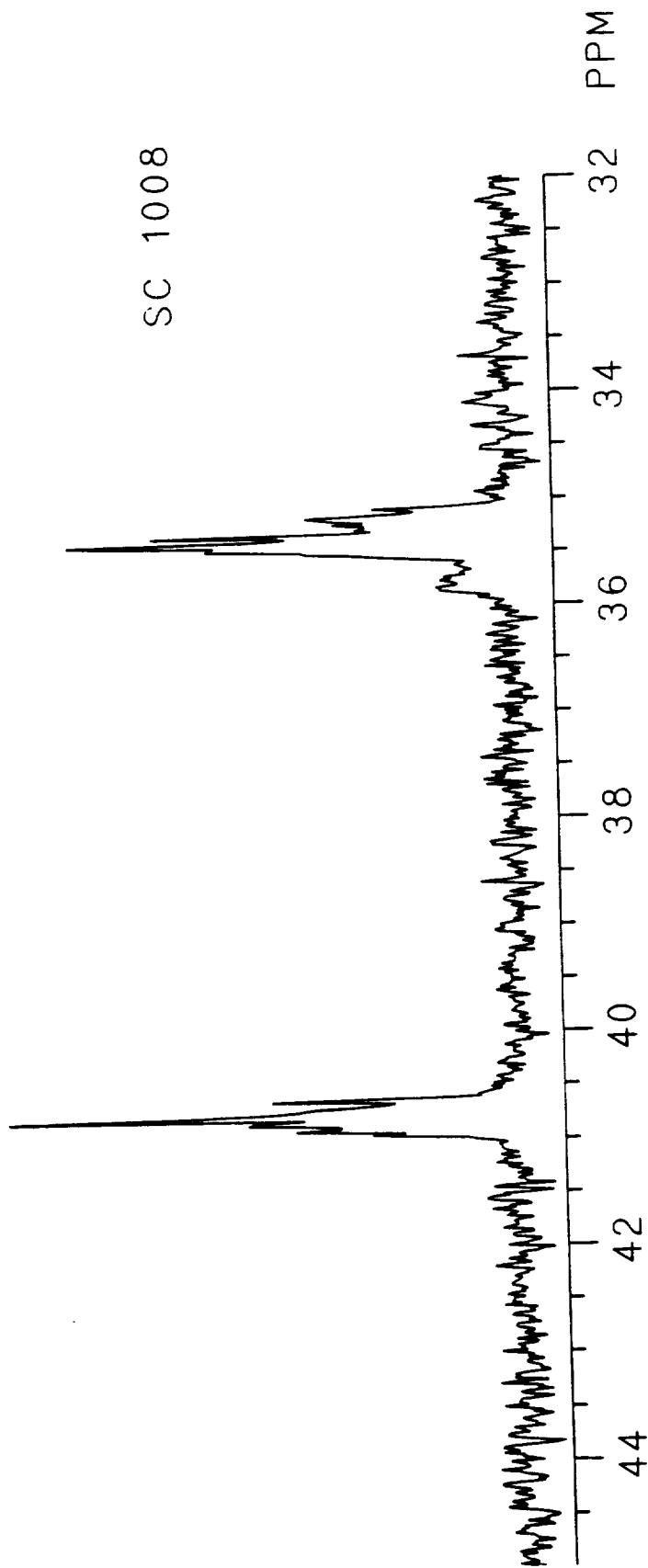


Ar CH₂ Ar

LD 91



SC 1008



ACKNOWLEDGMENTS

Ping Chao

Hercules Aerospace

State of Mississippi: QE-300 NMR Spectrometer

APPENDIX H

LAURIE RANDO

FINGERPRINTING

**Presented by: L. C. Rando
SPIP/ASRM Workshop**

May 14, 1992

FINGERPRINTING

Areas to be Discussed:

- **Purpose and Benefits**
- **Definitions**
- **Simple Versus Complex Materials**
- **Approach for a Complex Material**
- **Examples of Utilization**

FINGERPRINTING

Purpose:

- Control material integrity
- Detect and identify the origin of material variations
 - vendor or sub-tier level formulation changes
 - ingredient substitutions
 - mislabeled products
 - material degradation
 - component interactions
 - contamination
 - processing errors
- Provide baseline chemical profile of materials which conform to specifications

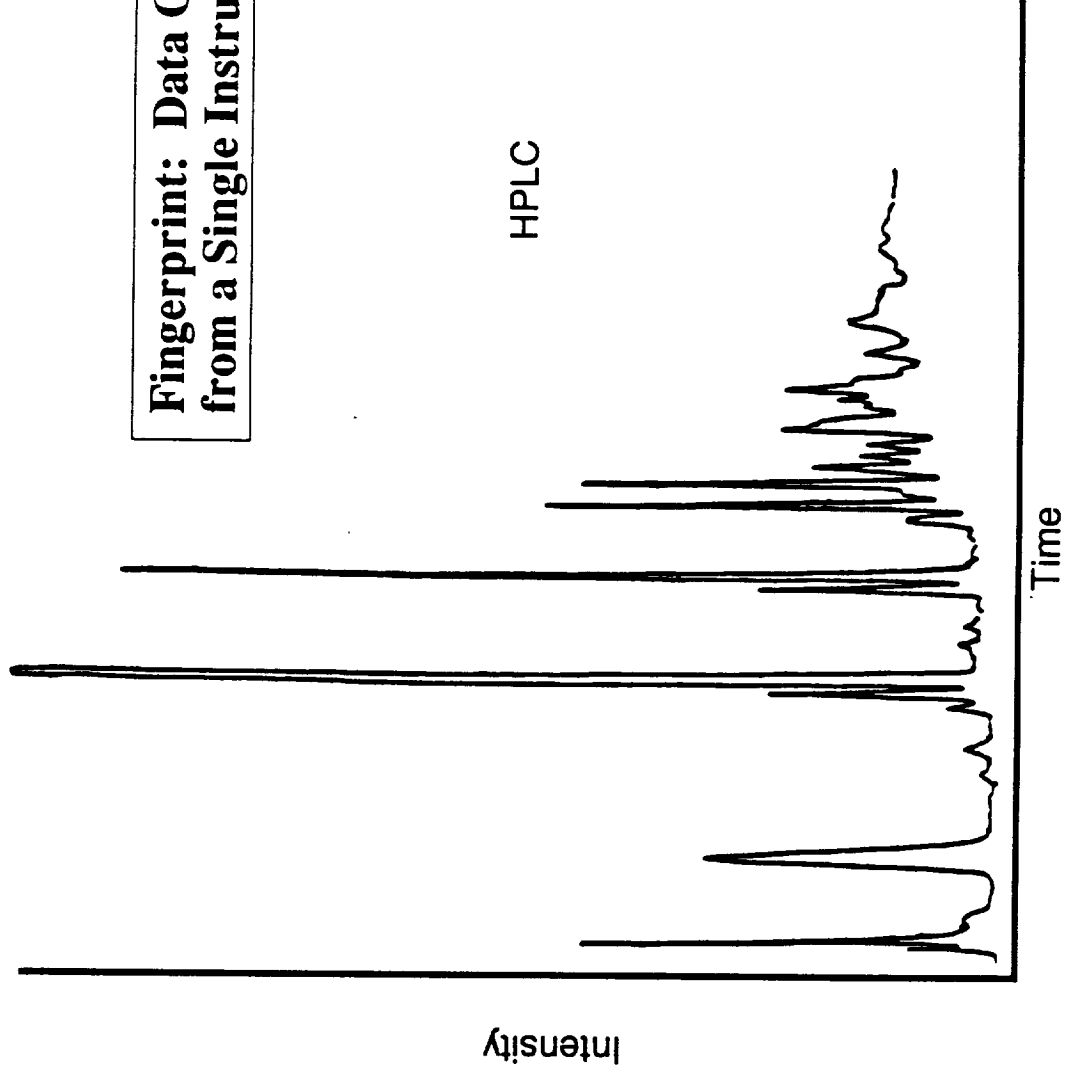
FINGERPRINTING

Benefits:

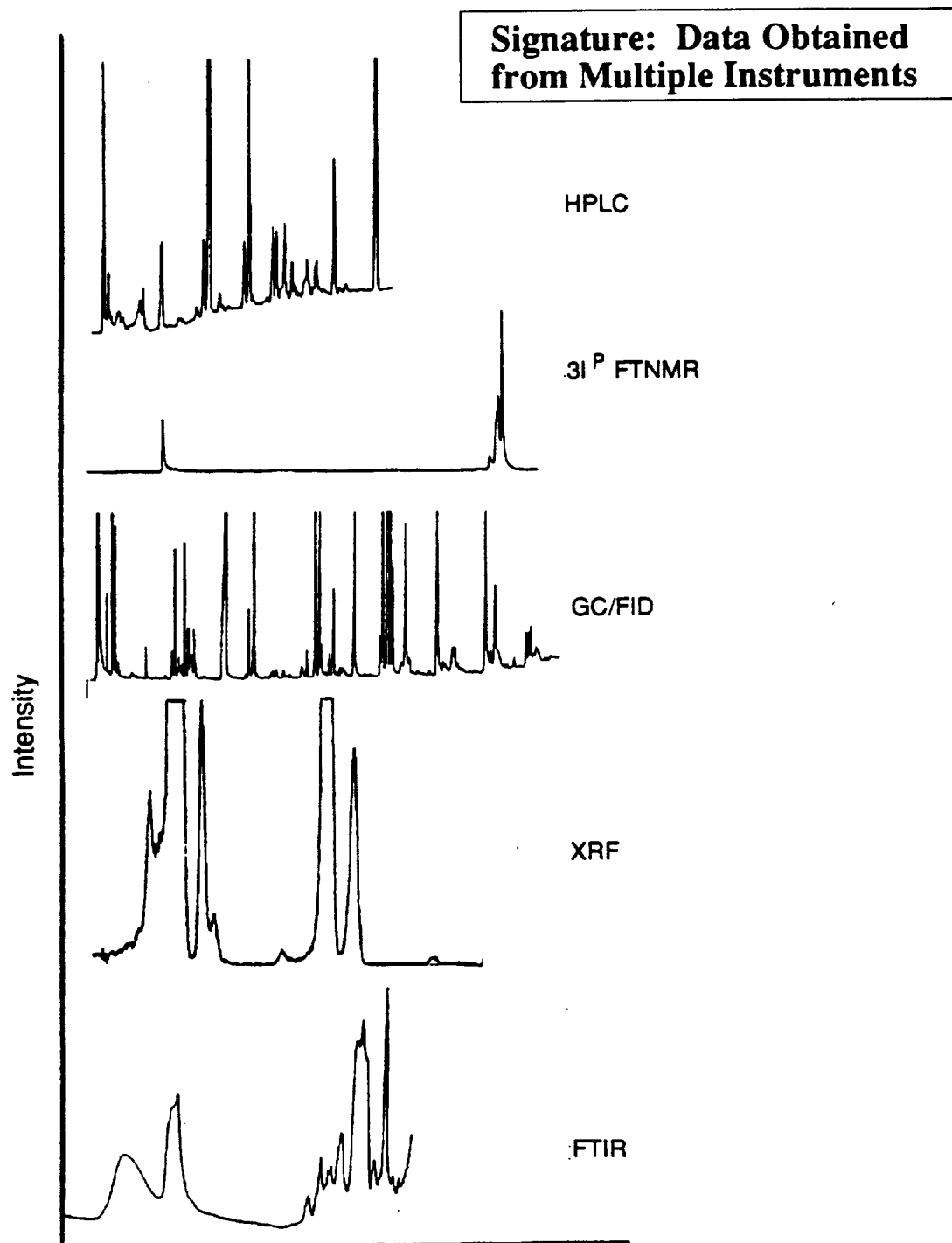
- Diagnostic
- Increased material reliability
- Expeditionary problem resolution
- Established reference libraries
- Cost-avoidance
- Automated sample analysis and calculations
- Increased safety
- Multipurpose methods and data
- Increased vendor communications

FINGERPRINTING

Fingerprint: Data Obtained
from a Single Instrument



FINGERPRINTING



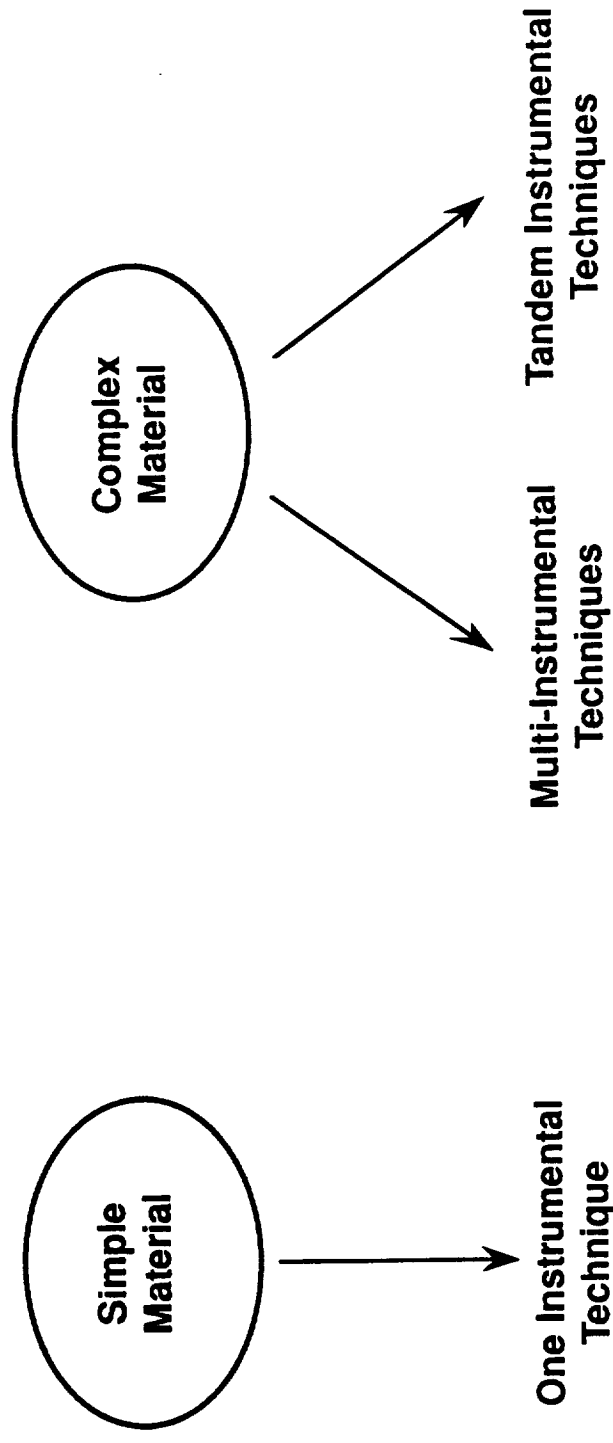
FINGERPRINTING

Questions to Determine Fingerprint Strategy:

- **Physical state of material?**
- **Bulk, surface, or micro analysis?**
- **Elemental, component, or functional group analysis?**
- **Organic, inorganic, or combination?**
- **One or more chemically/physically distinct phases?**
- **Single component or complex mixture?**
- **Major, minor, or trace components of interest?**
- **Interference or masking problems expected?**
- **Component separation required?**
- **Limited sample size?**
- **Qualitative or quantitative analysis?**
- **Required precision and accuracy?**
- **Resource availability?**
- **Required response time?**
- **Number of samples?**
- **Cost?**

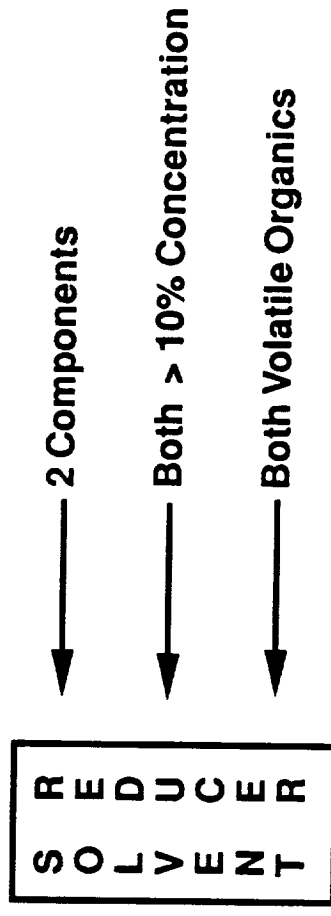
FINGERPRINTING

Fingerprinting Complexity:



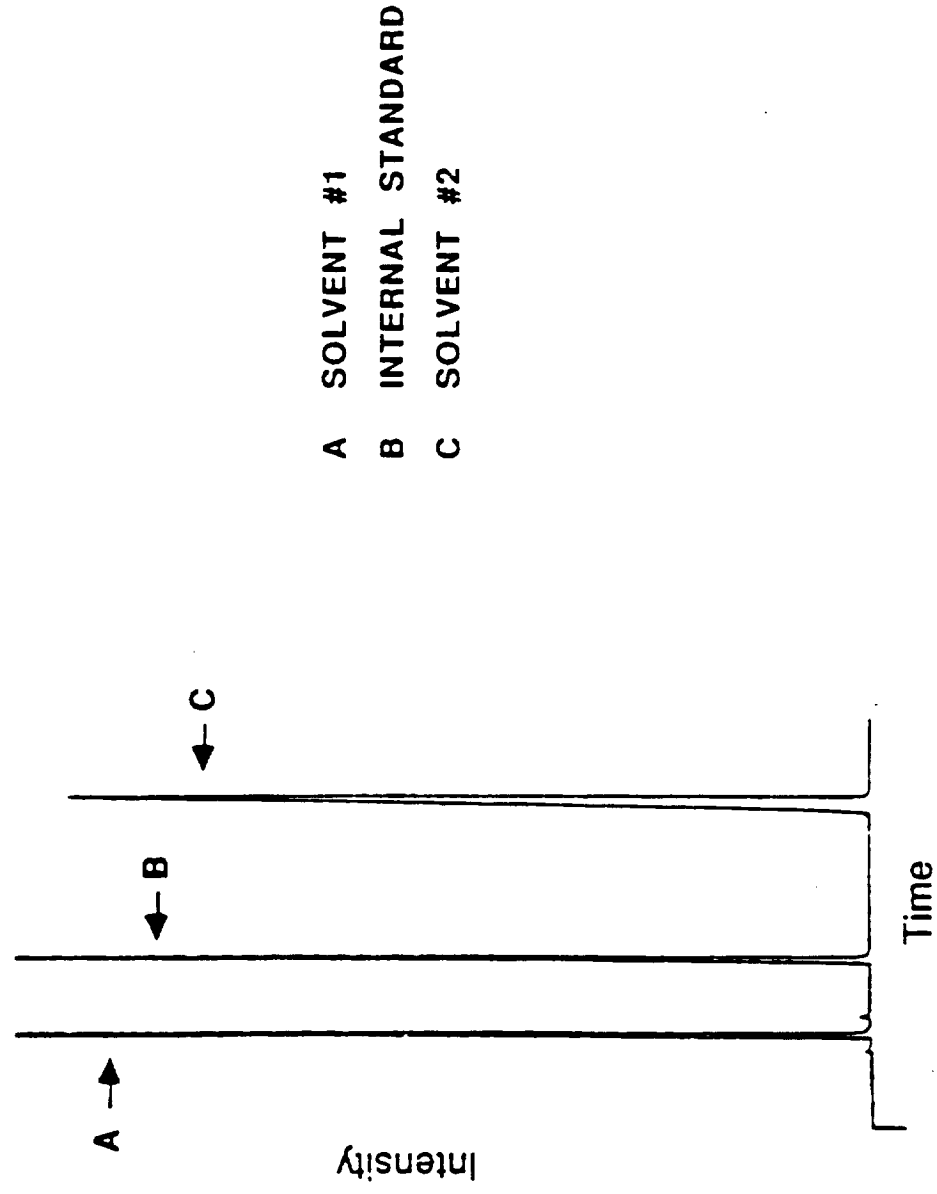
FINGERPRINTING

Example of a Simple Material



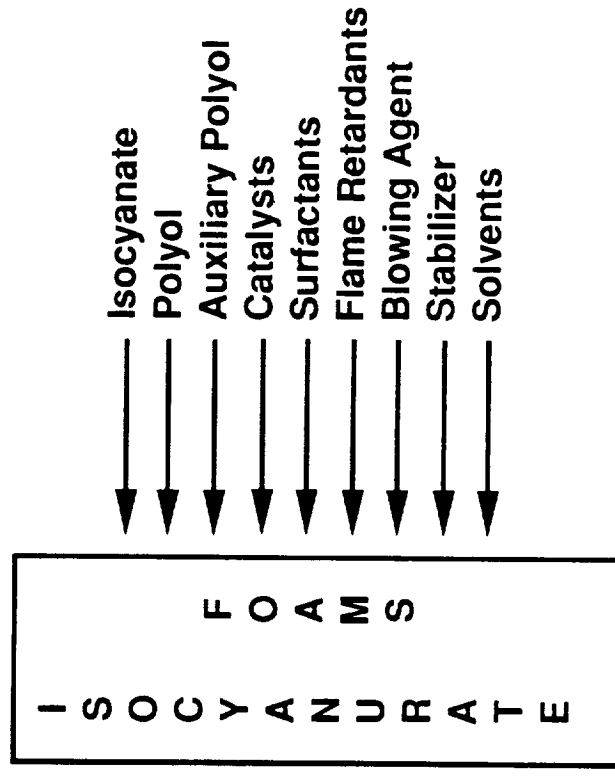
FINGERPRINTING

GC/FID Fingerprint of a Simple Material Solvent Reducer



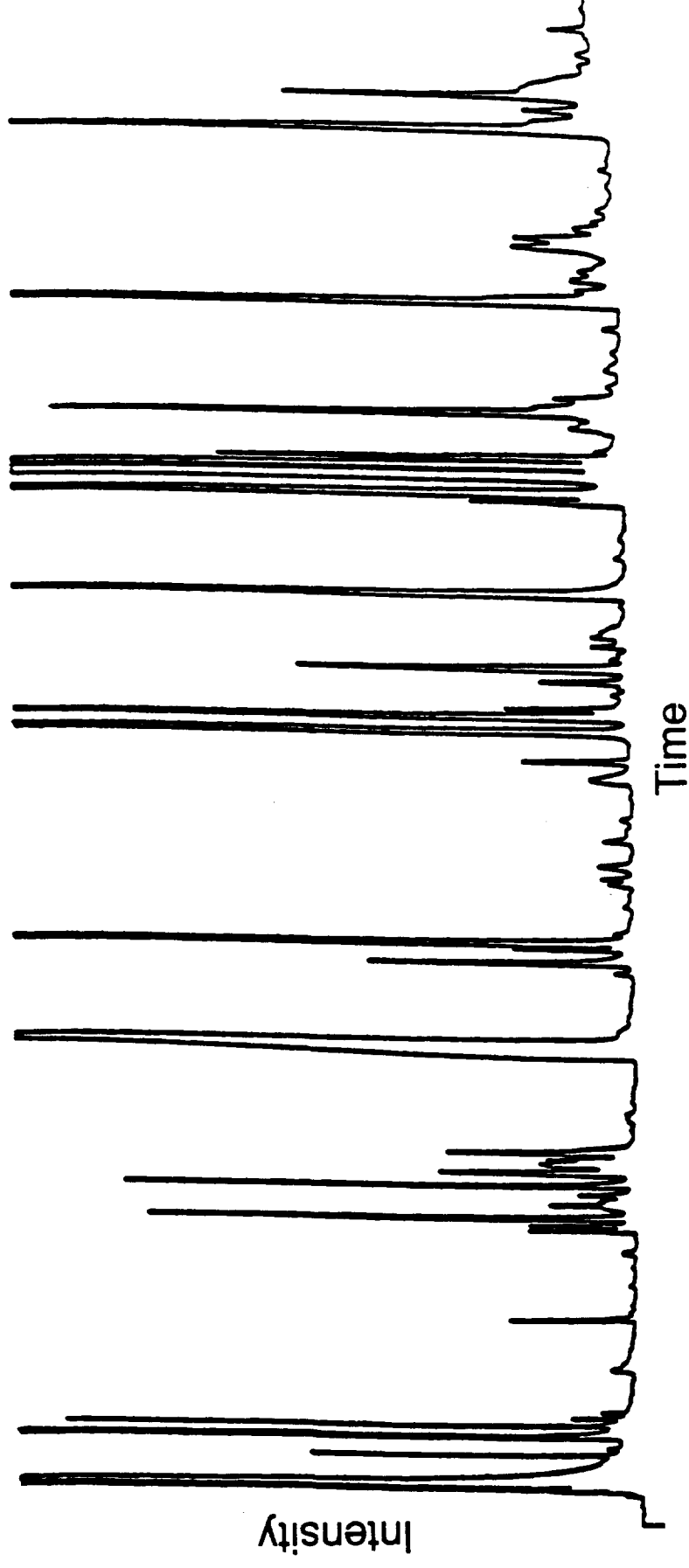
FINGERPRINTING

Example of a Complex Material



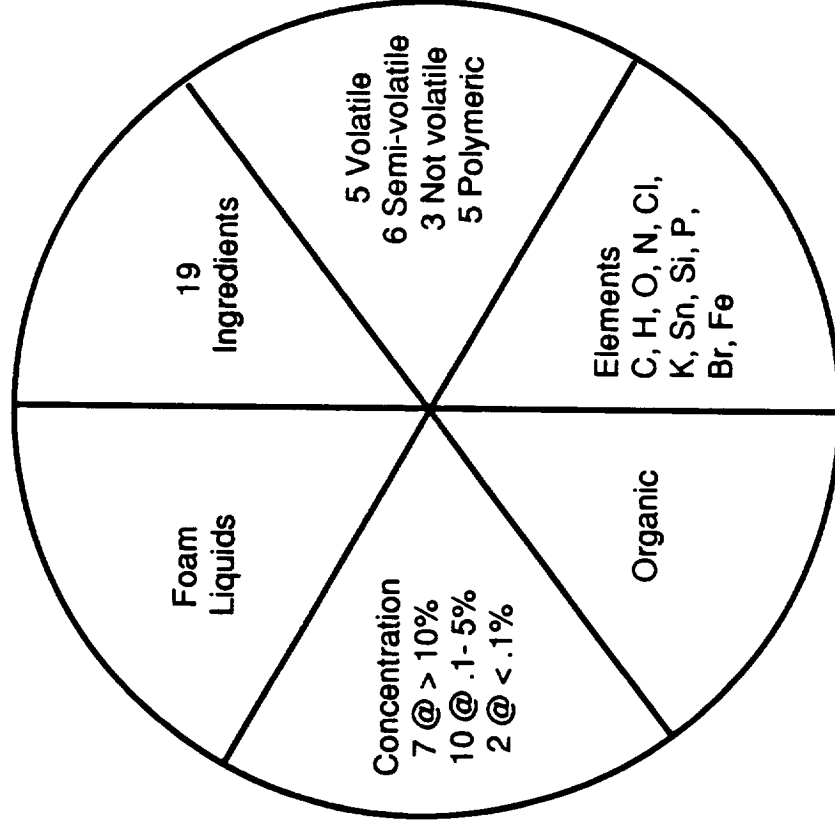
FINGERPRINTING

GC/FID Fingerprint of a Complex Material Component B of Foam

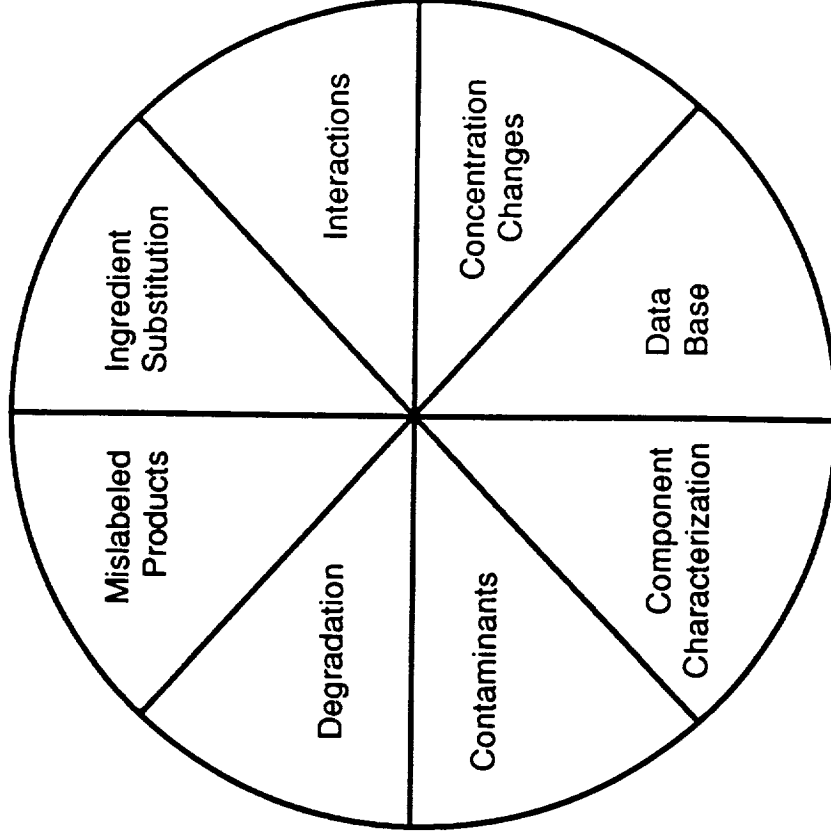


FINGERPRINTING

Example of a Complex Problem



Material Composition



Required Information

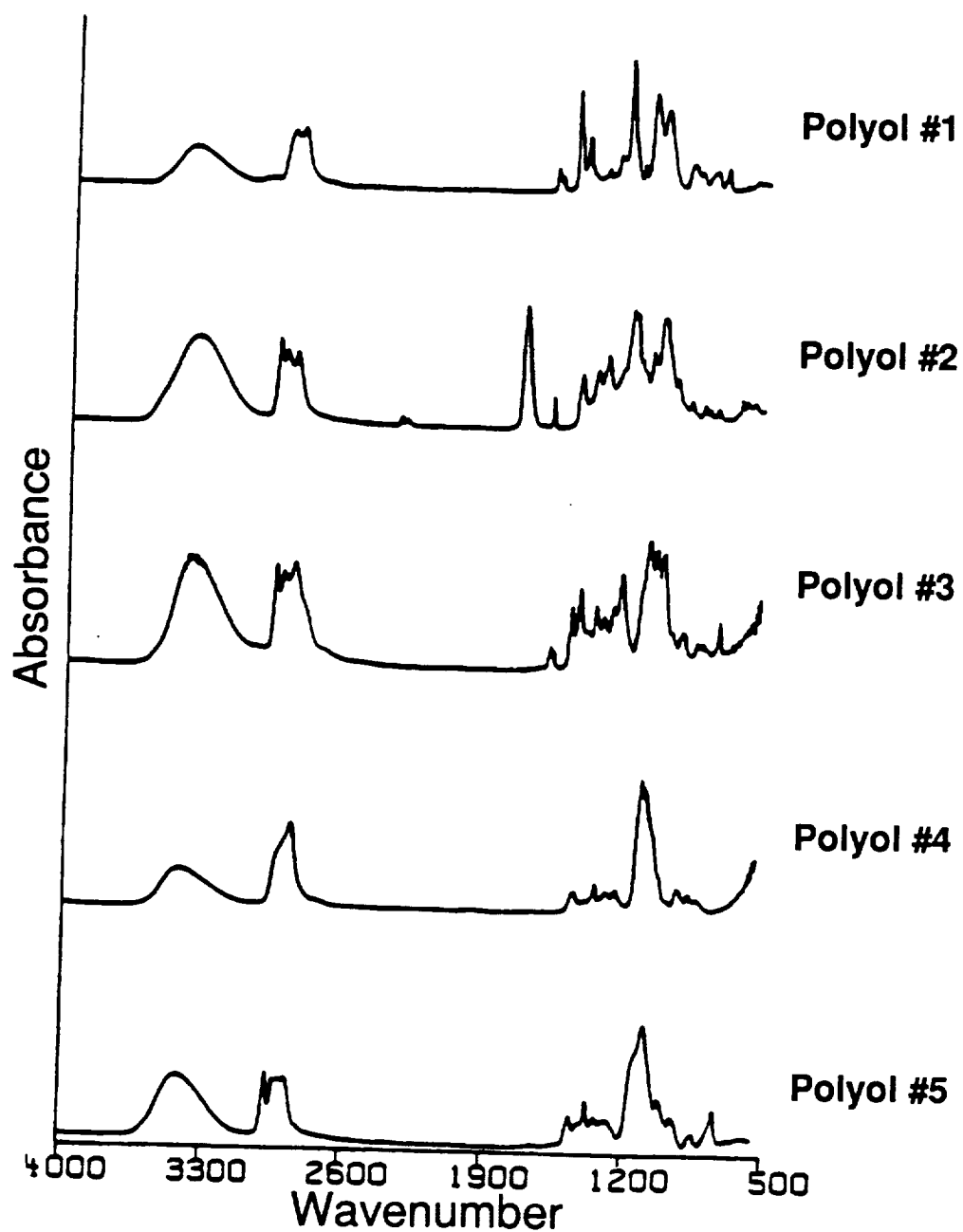
FINGERPRINTING

Approach for Complex Material:

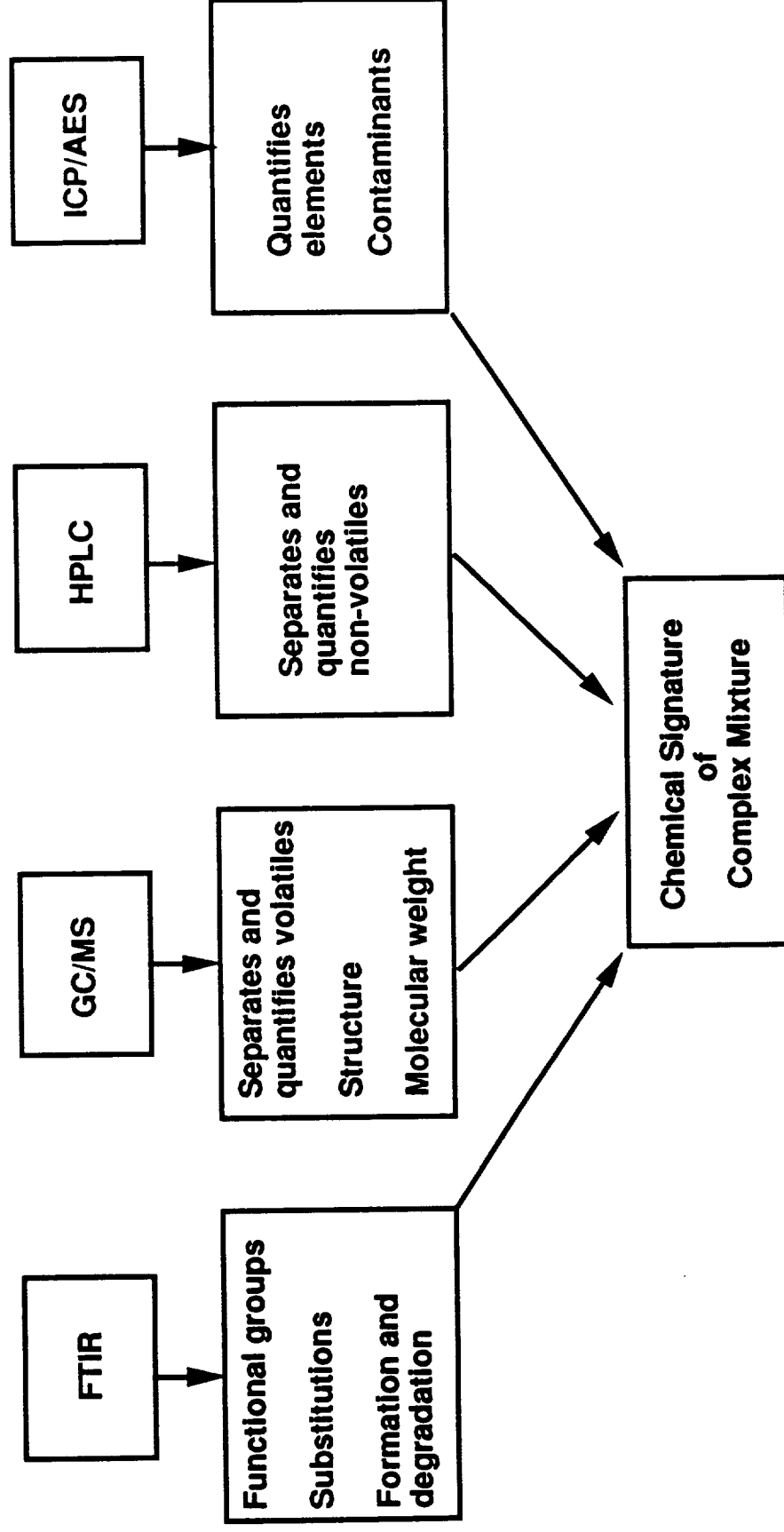
- Identify critical ingredients and potential contaminants related to the reactivity and performance of the material
- Select instrumental techniques that are compatible with the material, and sensitive and specific to the key ingredients and contaminants
- Develop instrumental analyses methods
- Statistically evaluate methods
- Fingerprint the individual ingredients and blends and compile data into a reference library
- Compile quantitative fingerprint databases
- Establish control charts

FINGERPRINTING

FTIR Library of Polyols



FINGERPRINTING



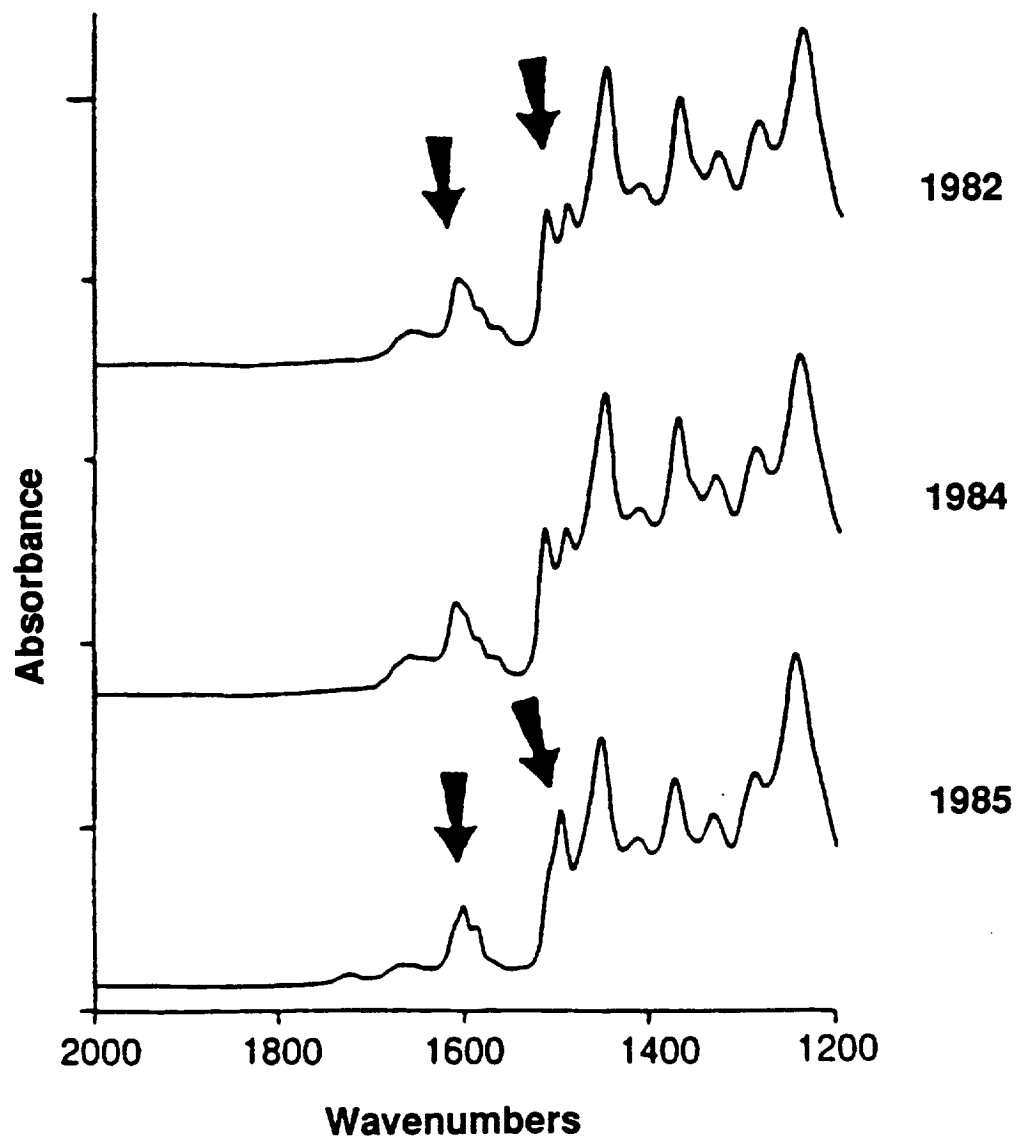
FINGERPRINTING

Utilization Areas:

- Receiving inspection
- Production processes
- Investigation of material failures
- Alternate and new material development
- Studies of off-gassing or degradation products
- Stability and shelf-life studies
- New supplier certification

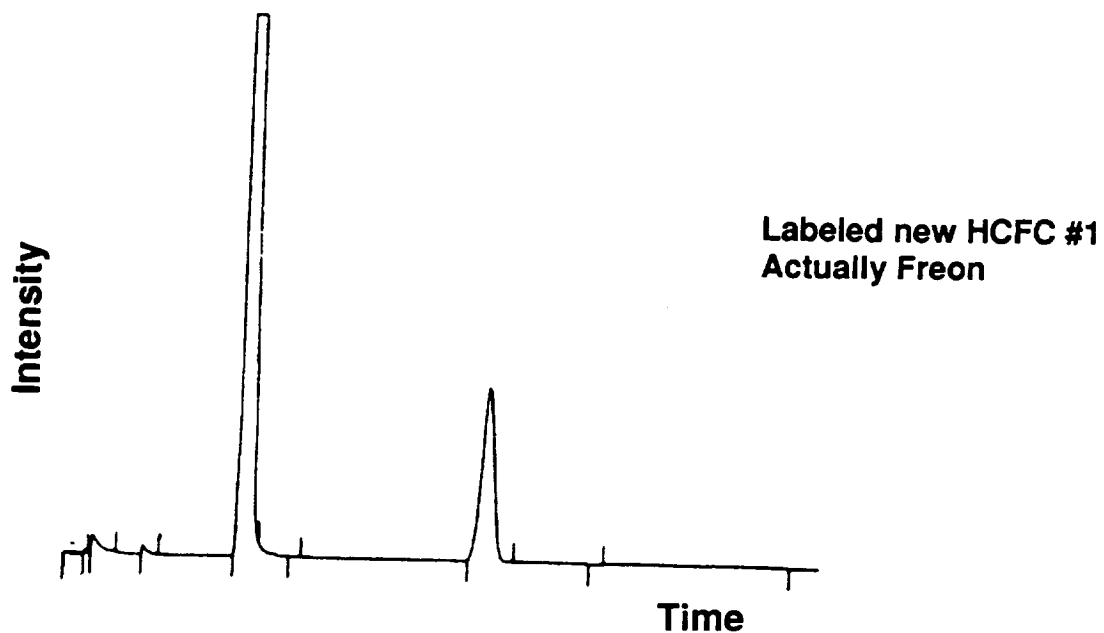
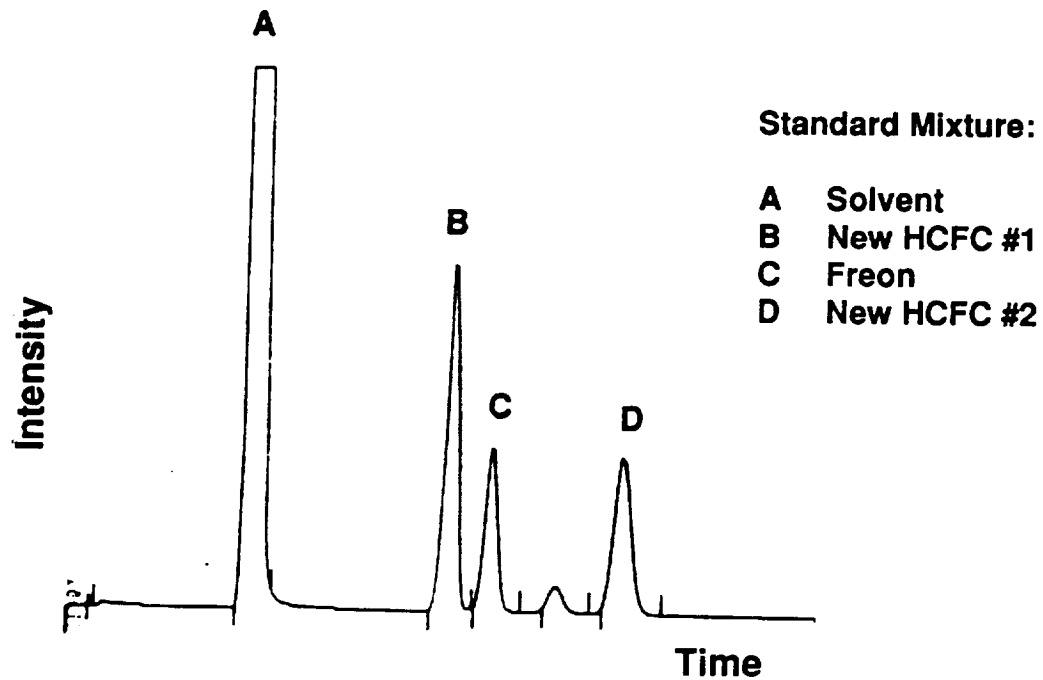
FINGERPRINTING

FTIR Detects Vendor Formulation Change Foam Component



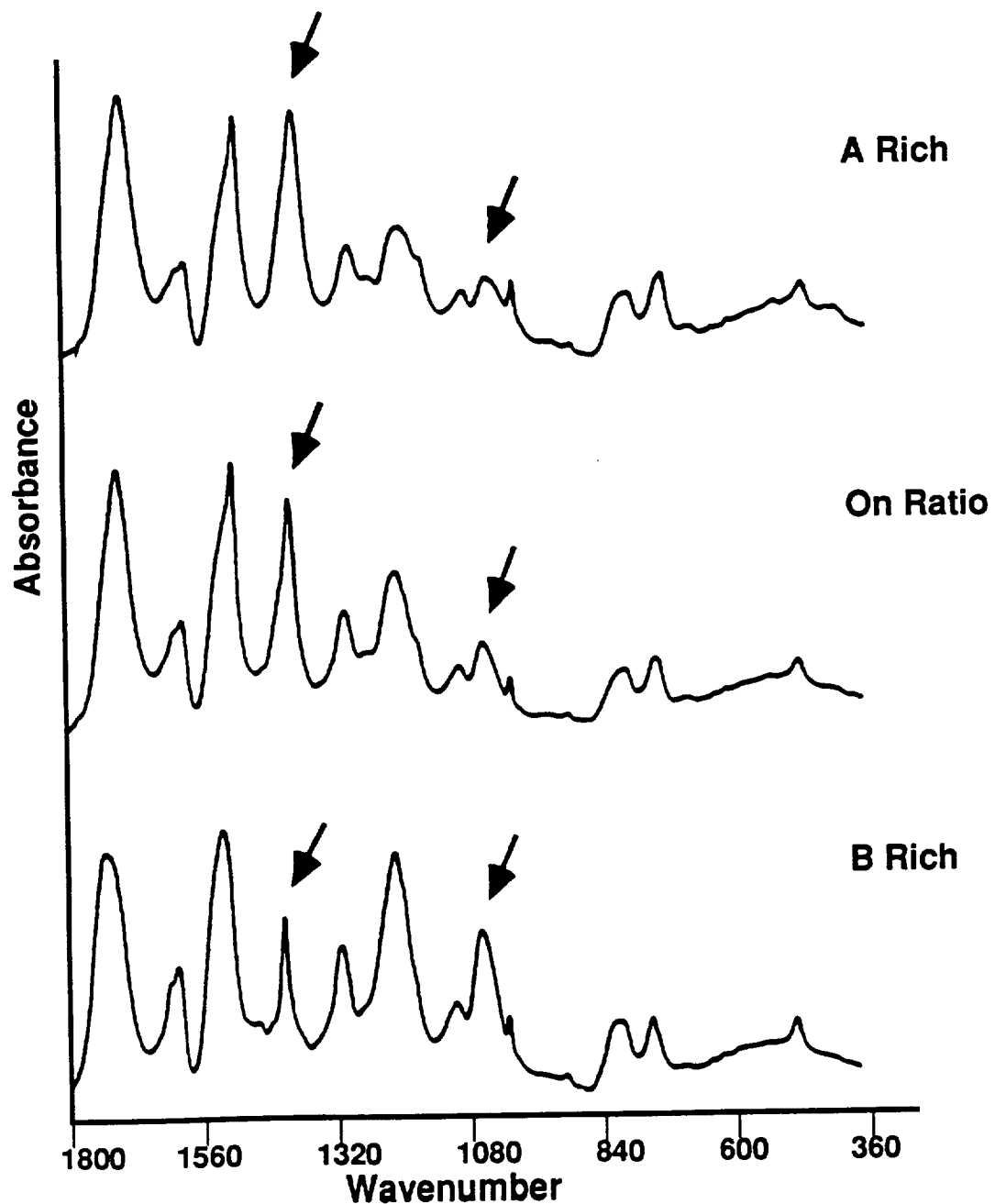
FINGERPRINTING

GC/TCD Detects Mislabeled Material Chlorofluorocarbons (CFC)



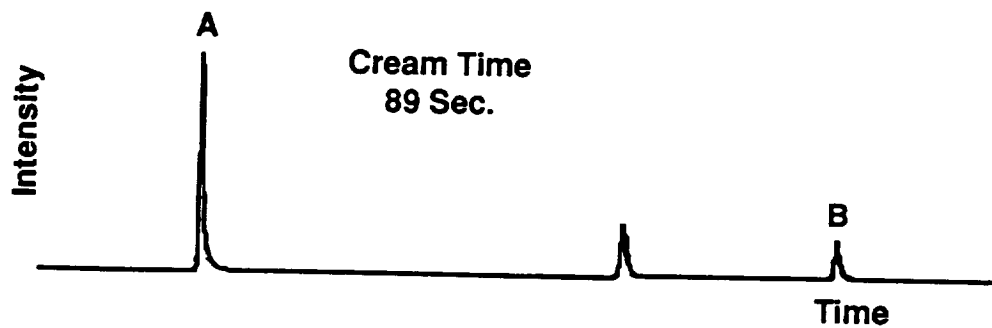
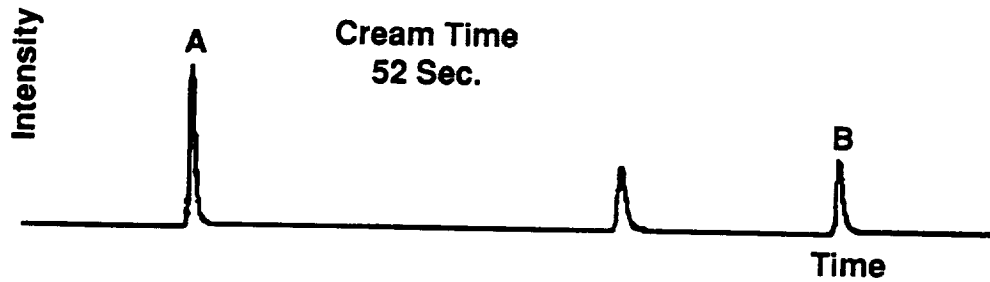
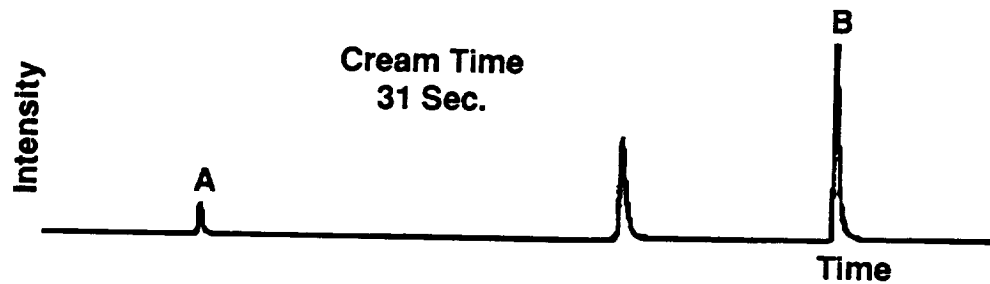
FINGERPRINTING

FTIR Detects Off-Ratio Application Cured Foam



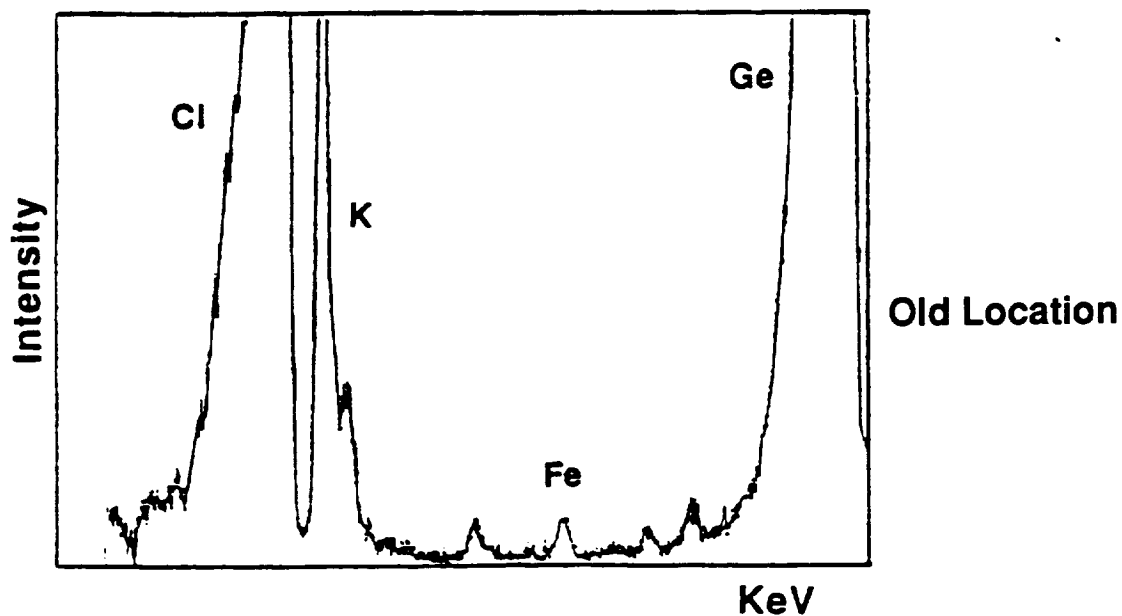
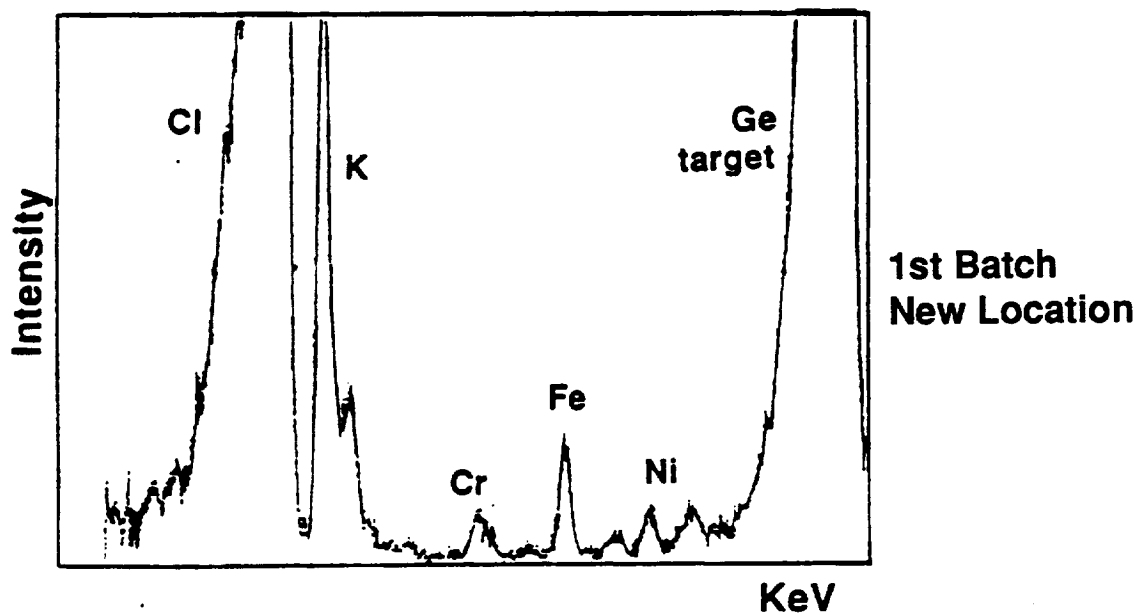
FINGERPRINTING

GC/SIM Detects Stabilizer Degradation In Foam



FINGERPRINTING

XRF Detects Vendor Contamination



ACRONYMS

CFC	Chlorofluorocarbon
HCFC	Hydrochlorofluorocarbon
FTIR	Fourier Transform Infrared Spectroscopy
FTNMR	Fourier Transform Nuclear Magnetic Resonance Spectroscopy
GC/FID	Gas Chromatography with Flame Ionization Detector
GC/MS	Gas Chromatography with Mass Spectrometer Detector
GC/SIM	Gas Chromatography with Selective Ion Monitoring
GC/TCD	Gas Chromatography with Thermal Conductivity Detector
HPLC	High Performance Liquid Chromatography
ICP/AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
XRF	X-ray Fluorescence Spectroscopy

APPENDIX I
ROMAN LOZA

Phenolic Resin Chemistry

SUMMARY OF WORK AT BP RESEARCH

TOPICS TO BE DISCUSSED

- Introduction
- Review of Phenolic Chemistry
- Analysis of 91-LD and SC-1008 at BP Research
 - NMR
 - FT-IR
- Aging studies (91-LD)
- Correlation of FT-IR data and NMR Data
- Commercial/Experimental Prepregs
 - Extraction/Analysis
 - NMR
 - FT-IR
 - DMTA
 - Experimental Prepreg Preparation
- Conclusions

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Phenolic Resin Chemistry

ACKNOWLEDGEMENTS

NMR: Robert D. Boyer (BP Research)

IR: Mary Ann S. Hazel (BP Research)

DMTA: Marty Mittleman (BP Research)

Prepreg: Mark Konarski (BP Chemicals)

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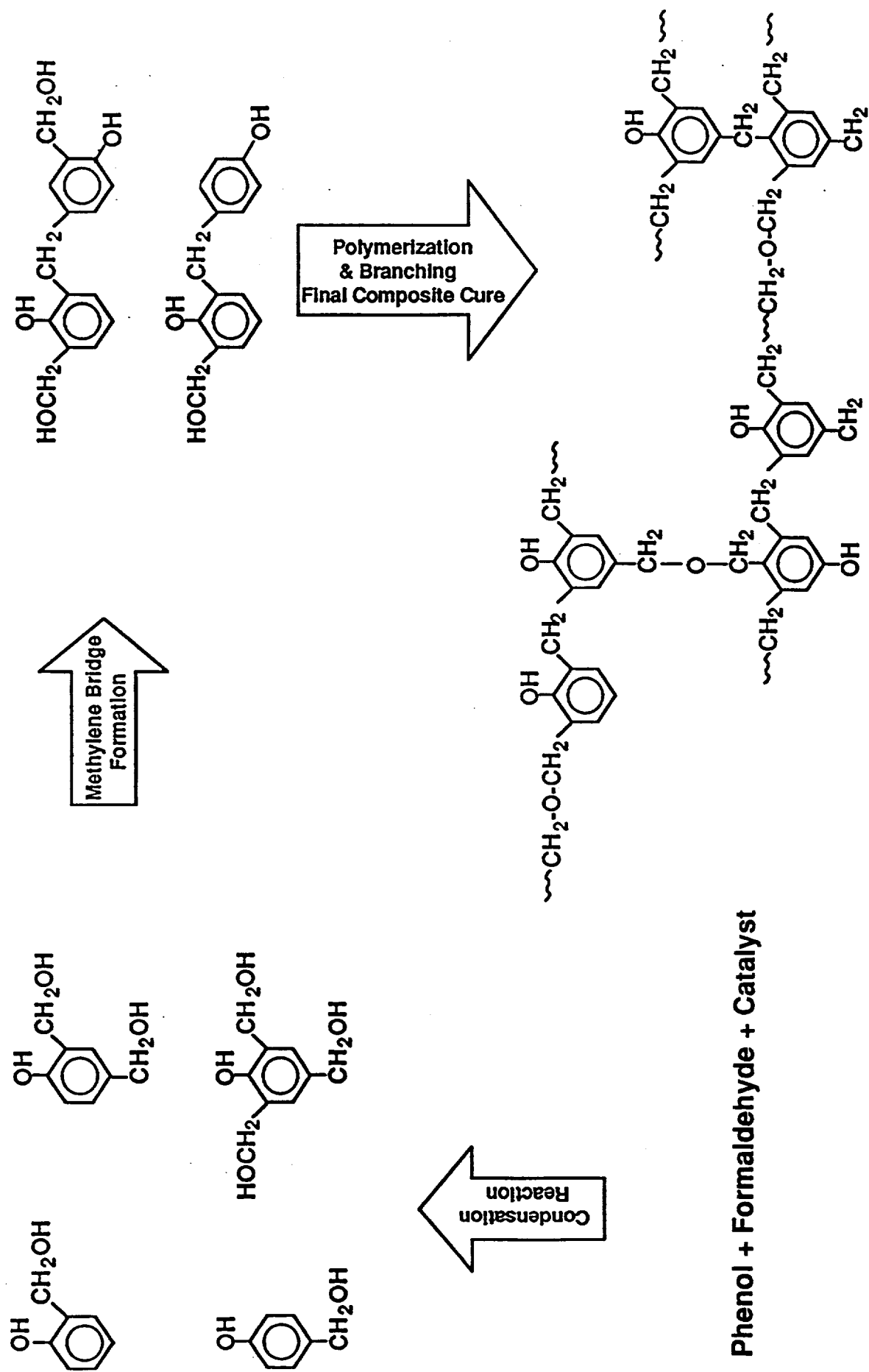
Phenolic Resin Chemistry

INTRODUCTION

- Develop NMR/IR spectroscopic techniques capable of quantifying the degree of advancement in phenolic resins.
- Compile NMR/IR data on phenolic resins used by F&M to establish a data base.
- Understand the chemistry of phenolic resins.

CHEMISTRY OF PHENOL FORMALDEHYDE RESINS

DIFFERENT STAGES OF CONDENSATION

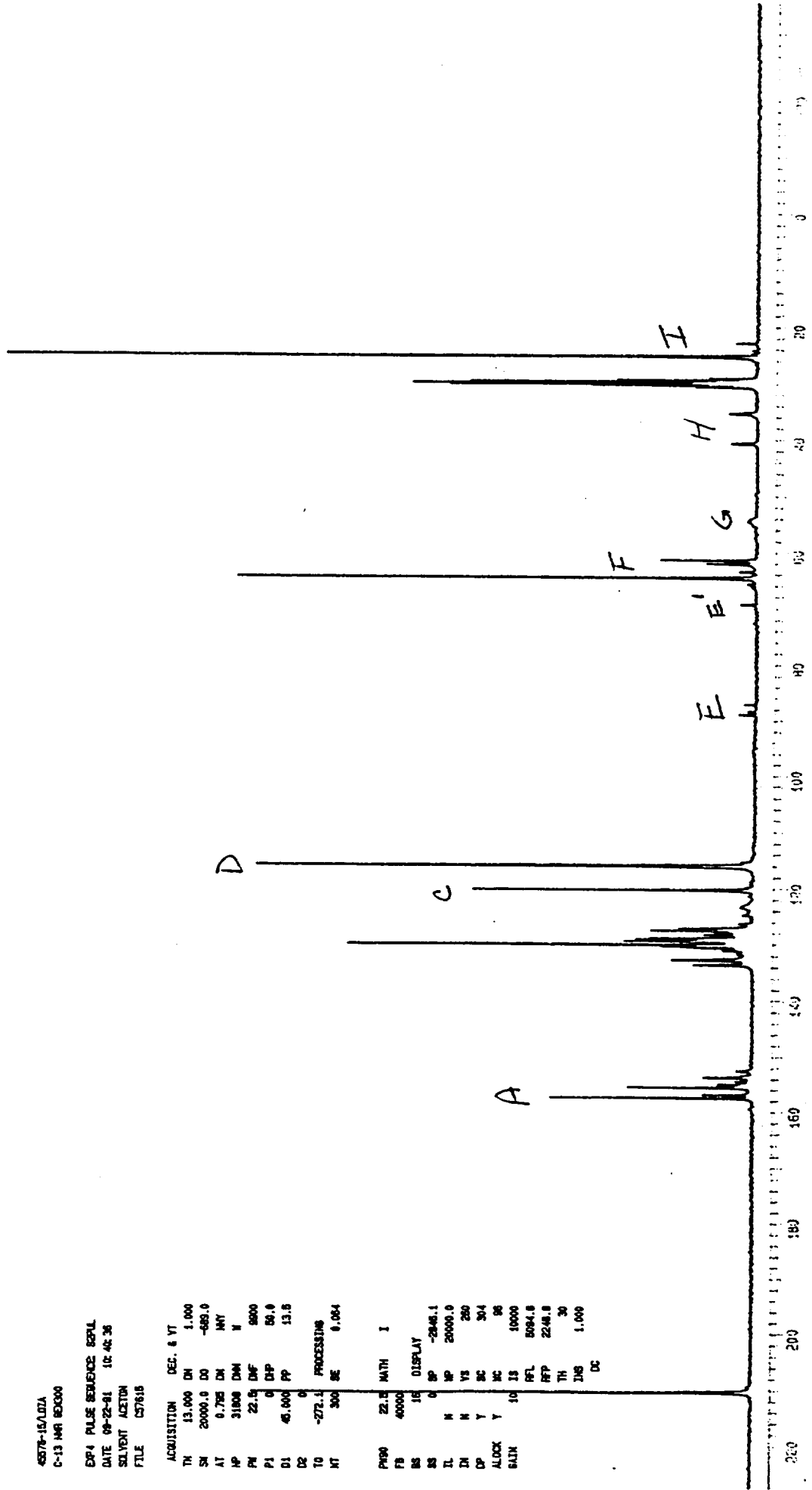


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C-13 NMR 820300

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DATE 09-22-81 10:46:36
SOLVENT ACETON
FILE C57815

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ALOCK Y 96
SALIN 10 13 10000
PFL 5094.8
PFP 2248.8
TH 30
IMS 1.000
DC



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Phenolic Resin Chemistry

PHENOLIC RESINS
STRUCTURAL INFORMATION

C-13 Nmr Assignments

Group	Resonance (ppm)	Assignment
A	160-152	Aromatic C-O (phenol carbons) including unsubstituted phenol (ca.157.7-157.3).
B	134-126	Substituted aromatic, unsubstituted meta-aromatic.
B'	126-122	ortho-Substituted aromatic (tentative).
C	121-119	para-Unsubstituted.
D	118-116	ortho-Unsubstituted.
E	90-86	-OCH₂O- (formals).
E'	70-65	ArCH₂OR (R = formal).
F	65-60	Ar-CH₂OH and isopropanol (IPA).
G	60-52	Amine derivatives (tentative).
H	42-32	Ar-CH₂-Ar
I	26-22	Isopropyl methyl groups (isopropanol and isopropyl formals).

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PHENOLIC RESINS STRUCTURAL INFORMATION

C-13 Nmr Ratios

NMR Ratios are used in Quantitative Analysis:

Formaldehyde Carbon Distribution (mole %).

-OCH₂O- (Formal)

ArCH₂OR (Methylol)

ArCH₂Ar (Methylene bridge)

ArCH₂N- (Amine bridge)

Formaldehyde Carbon (CH₂)/Phenolic Carbon (C-O).

Methylol Index

Methylene Bridge Index

IPA/Total Phenolic Carbon.

Unsubstituted Phenolic Carbon (C-O)/Total Phenolic Carbon (C-O).

Degree of ortho/para-substitution (with/without unsubstituted phenol).

NMR Ratios are useful for estimating compositional changes:

Lot to Lot for specific resin.

During storage/aging (no time limit).

Neat resin to prepreg.

Between resin types.

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PHENOLIC RESINS STRUCTURAL INFORMATION

Ir Peak Ratios

IR Peak Ratio	Assignment
1024/1000	Ether (e.g. formal) to aromatic alcohol (methylol).
826/1000	Phenol and para-substituted aromatic to aromatic alcohol.

IR assignments are somewhat ambiguous (overlap possible) but still can be used for quantification of resin advancement:

Resin advancement on storage/aging (0-20 days @ RT).

Resin advancement and compositional changes -- lot to lot.

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Phenolic Resin Chemistry

**COMPARISON OF PHENOLIC RESINS:
91-LD AND SC-1008**

	91-LD	vs. SC-1008
<u>Isopropanol/Phenolic (C-O):</u>		
(mole ratio)		Different
<u>Formaldehyde/Phenolic (C-O):</u>		
(mole ratio)		Similar
<u>Formaldehyde Carbon (Mole %):</u>		
-OCH ₂ O- (Formal)		Similar
ArCH ₂ OR (Methylol)		Different
ArCH ₂ Ar (Methylene bridge)		Different
ArCH ₂ N- (Amine bridge)		Different
<u>Aromatic Ring Substitution:</u>		
% ortho-Substitution (w/o PhOH)		Similar
% para-Substitution (w/o PhOH)		Different
<u>Infrared Ratio:</u>		
1024/1000		Different
826/1000		Similar

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Phenolic Resin Chemistry

AGING STUDIES -- 91-LD

Conditions: Room Temperature (21.5° C)

Time -- 1 to 90 days

Monitoring:

IR: -1024/1000 and
 - 826/1000 peak ratio.

NMR: -Formaldehyde CH₂ distribution
 -Phenol substitution.

Viscosity: -Brookfield viscosity.

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Phenolic Resin Chemistry

AGING STUDIES -- 91-LD

Nmr Results:

Formaldehyde Distribution (mole %):

-OCH ₂ O- (Formal)	Drops to zero.
ArCH ₂ OR (Methylol)	Increases then decreases
ArCH ₂ Ar (Methylene bridge)	Increases linearly
ArCH ₂ N- (Amine bridge)	No Change

% Unsubstituted Phenol (PhOH):

Decreases then no change.

Degree of ortho/para-substitution (w/o PhOH):

% Ortho-substitution	increases then no change.
% Para-substitution	increases (two rates --faster then slower).

Formaldehyde (CH₂)/Total Phenolic (C-O):

No change.

IPA/Total Phenolic C-O:

No change.

0-4

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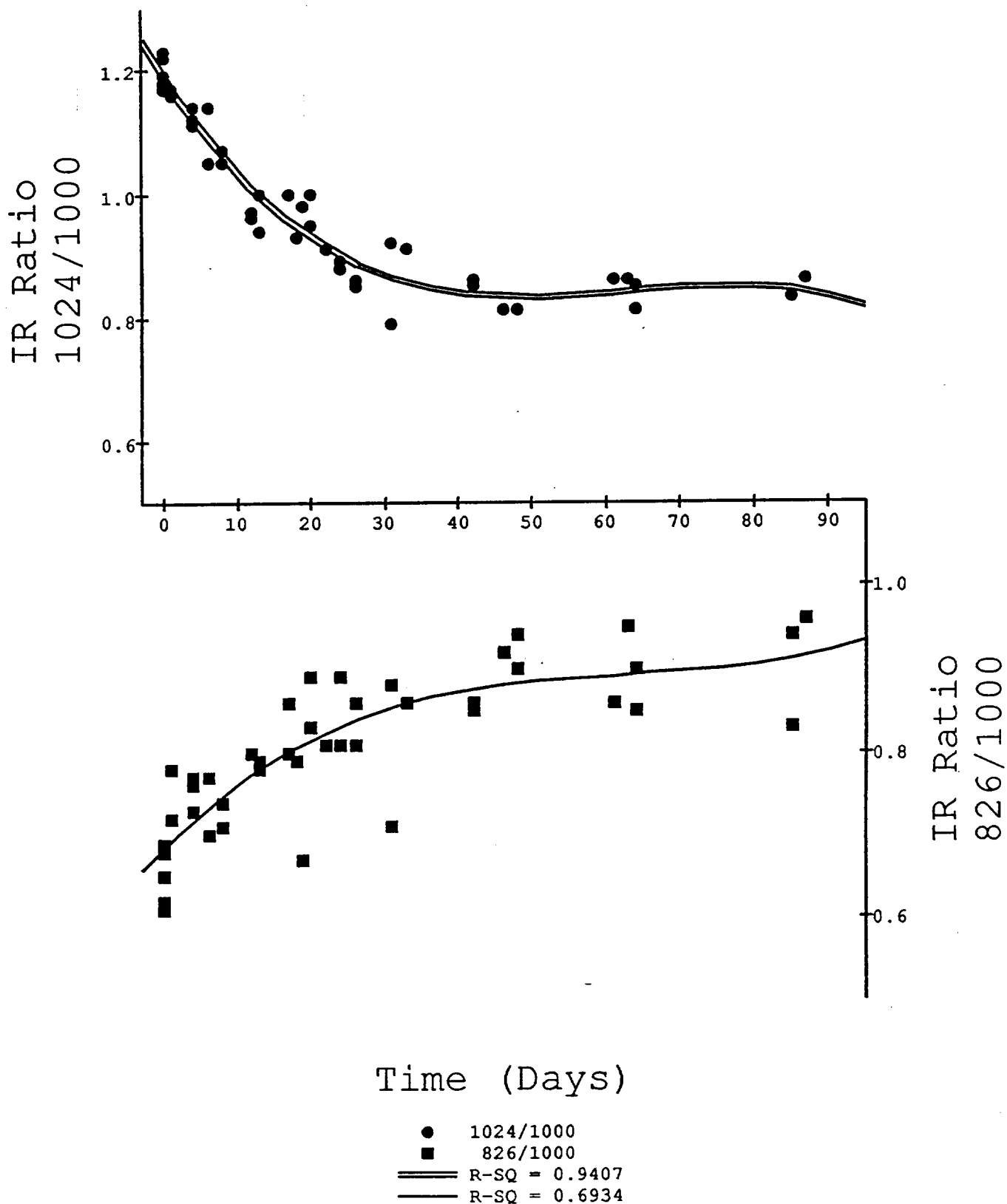
Phenolic Resin Chemistry

AGING STUDIES -- 91-LD

IR Results:

1024/1000 -- Decreases with time then levels off

826/1000 -- Increases with time then levels off.

Aging Studies of 91-LD
Ir Data Summary

Equation for line:

$$1024/1000 = -1.65e-06 \cdot X^{**3} + 3.10e-04 \cdot X^{**2} - 1.86e-02 \cdot X + 1.19$$

$$826/1000 = +6.98e-07 \cdot X^{**3} - 1.32e-04 \cdot X^{**2} + 8.81e-03 \cdot X + 0.69$$

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Phenolic Resin Chemistry

AGING STUDIES -- 91-LD

Brookfield Viscosity Results:

Relative viscosity

(viscosity @ time= t days/viscosity @ time=1 day)

increases linearly with time.

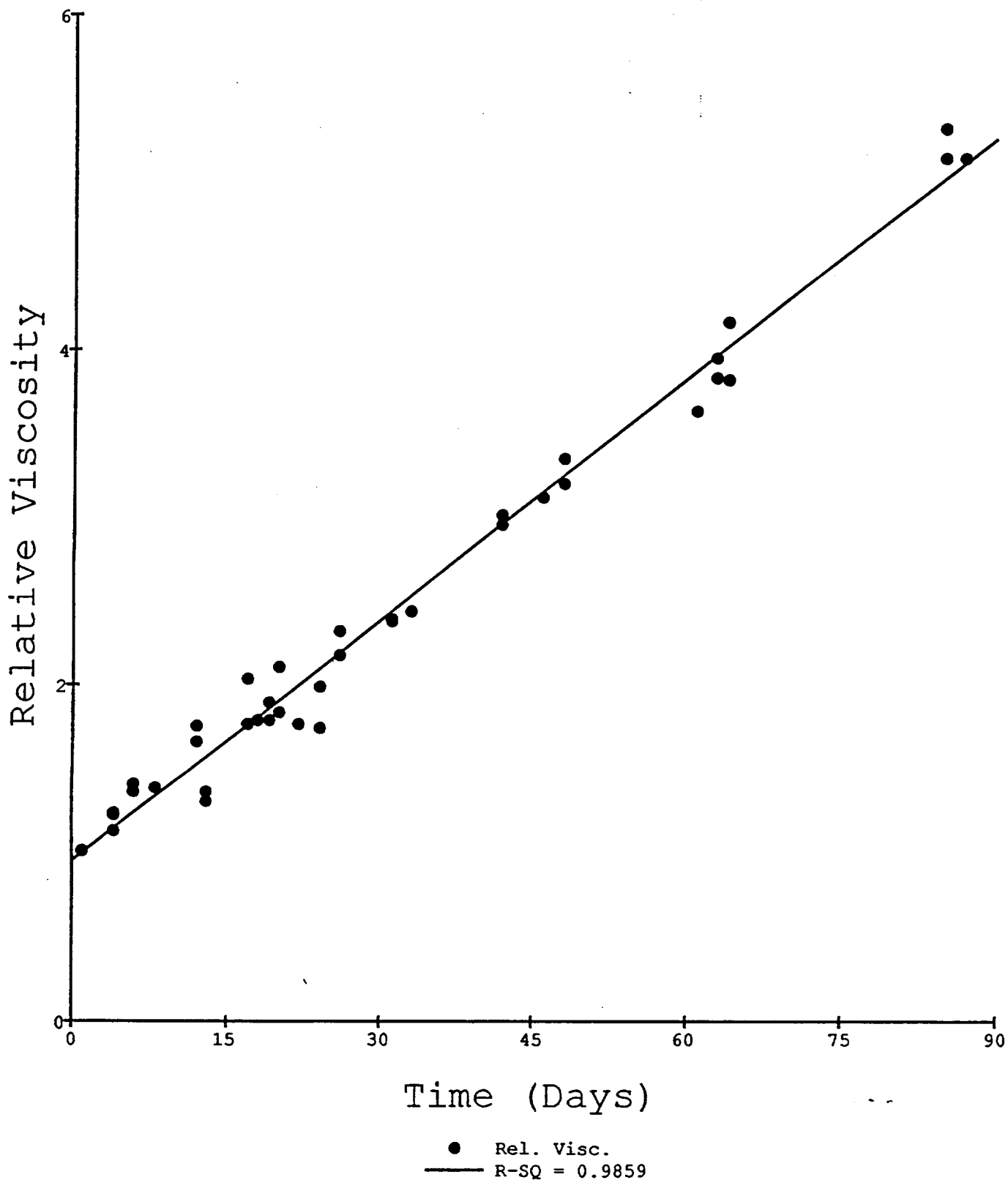
100% at 1 day

200% at 22 days

300% at 43 days

400% at 63 days

Aging Studies of 91-LD
Relative Viscosity vs. Time



Equation of line:

Rel. Visc. = $4.78 \times 10^{-2} \times X + 0.9527$

Rel. Visc. = (Visc. @ time=X days)/(Visc. @ time=1 day)

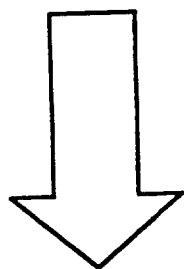
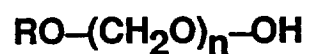
Rel. Visc. data has generated from 5 different resins.

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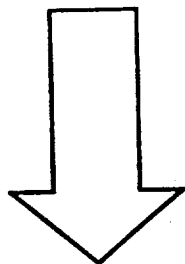
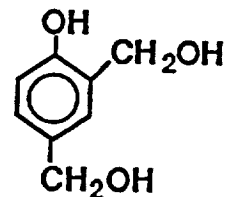
Phenolic Resin Chemistry

CHEMISTRY OF PHENOL FORMALDEHYDE RESINS
ROOM TEMPERATURE AGING
PROPOSED REACTION SEQUENCE

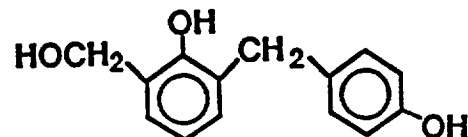
Unreacted Formaldehyde as "Formals"



"Methylols"



"Methylene Bridged" Phenolics



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Phenolic Resin Chemistry

CORRELATION OF FT-IR DATA WITH NMR DATA

Aging Studies -- 91-LD

Decrease in unreacted formaldehyde (formals) content
correlates with

Decrease in 1024/1000 ratio ($R^2 = 0.9317$) and

Increase in 826/1000 ($R^2 = 0.7619$)

As Received 91-LD

Decrease in unreacted formaldehyde (formals) content
correlates with

Decrease in 1024/1000 ratio ($R^2 = 0.7885$).

As Received SC-1008 (Including Experimental Resins)

Decrease in unreacted formaldehyde (formals) content
correlates with

Decrease in 1024/1000 ratio ($R^2 = 0.9171$) and

Increase in 826/1000 ($R^2 = 0.8191$)

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Phenolic Resin Chemistry

COMMERCIAL PREPREG EXTRACTION/ANALYSIS

NMR and FT-IR Analysis

General changes occurring in phenolic resin during prepreg preparation:

Methylene distribution changes.

Methylol content decreases.

Aromatic **ether-bridges** appear?

Methylene bridge content increases.

Ortho-para linkages predominate.

Ortho/para-substitution increases.

Unreacted phenol content decreases.

Formaldehyde/Phenolic mole ratio increases.

The 826/1000 FT-IR ratio increases

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Phenolic Resin Chemistry

91-LD PHENOLIC RESIN
AS RECEIVED, AGED AND FROM PREPREG

	FRESH	AGED 60 D	PREPREG
<u>Formaldehyde/Phenol:</u>			
(mole ratio)	nominal	nominal	+ 20%
<u>Formaldehyde Derivative:</u>			
-OCH ₂ O- (Formal)	nominal	none	none
ArCH ₂ OR (Methylol Index)	62	61	35
ArCH ₂ Ar (Methylene Bridge Index)	16	23	37
p-p'/o-p	1.2	1.3	0.6
<u>Aromatic Ring Substitution:</u> (excluding Unreacted Phenol)			
% ortho-Sub. (w/o PhOH)	nominal	+07%	+19%
% para-Sub. (w/o PhOH)	nominal	+16%	+33%
<u>Mole% unreacted PhOH:</u>	nominal	-20%	-80%
<u>Infrared Ratio:</u>			
826/1000	0.69	0.89	0.95

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Phenolic Resin Chemistry

DMTA ANALYSIS OF PREPREGS

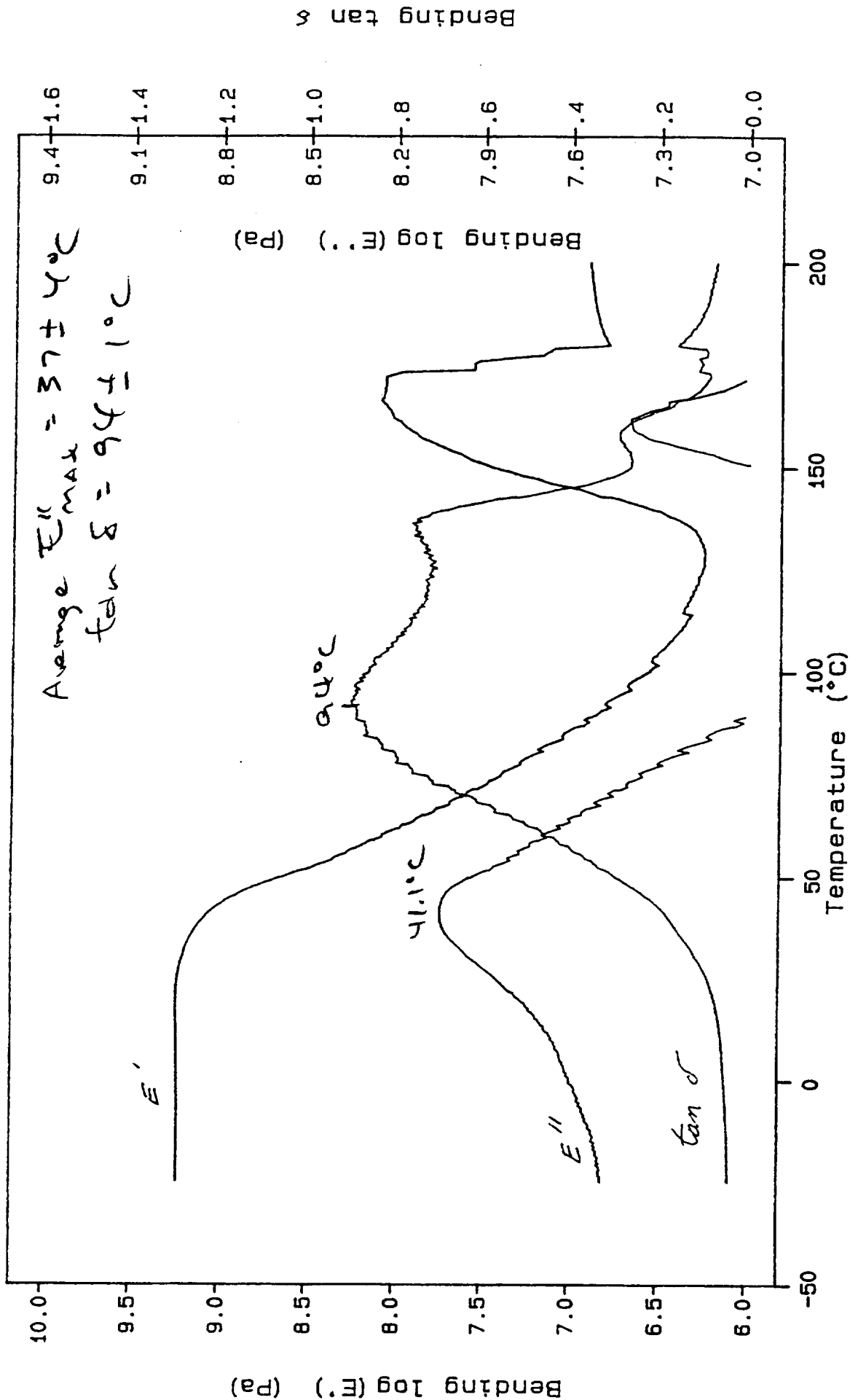
DMTA:	Dynamic Mechanical Thermal Analysis
What is measured:	Rheological properties as a function of temperature. Storage modulus (E') Loss modulus (E'') $\tan \delta = E''/E'$
Data used:	Transition temperatures: E'' max temperature $\tan \delta$ max temperature
Prepreg information:	Temperature for maximum pliability. Glass transition temperature. Cure monitoring.

DMTA

Head: Combined 300°C
BP - America

SMPL ID : 184/3/REP
FREQ : 10
DIM: 1, 6, 8, .79
CORRECTED DELTA=-.617

DATE RUN: Oct/29/1991
DISP : 2
COMMENT: LOZA



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Phenolic Resin Chemistry

EXPERIMENTAL PREPREG PREPARATION

FM5055B phenolic mix was prepregged onto glass fabric.

Very mild conditions were used.

Resin content lower than on carbon fabric.

Pregreg was cut into smaller pieces and heated in an air circulating oven.

Variables examined:

time, temperature, resin age, prepreg age.

Responses measured:

Flow, Vols., Drape

Nmr, FT-IR, DMTA performed on selected specimens.

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Phenolic Resin Chemistry

EXPERIMENTAL PREPREG EXTRACTION/ANALYSIS

Results

	Sample No.:			
	1	2	3	4
STAGING CONDITIONS:				
Temperature/Time	A/A	A/B	B/A	B/B
PREPREG PROPERTIES:				
Soluble Resin (%)	100	96	100	62
Flow (%)	12.2	8.4	10.4	1.4
Drape (0-10)	9	4	5	2
DMTA TRANSITION TEMPERATURES:				
E" max (°C)	19	30	18	85
tan δ max (°C)	39	40/81	39/92	124
IR RATIOS:				
1024/1000	0.90	0.97	0.94	1.00
828/1000	0.80	0.82	0.80	1.05
NMR DATA:				
Methylol Index	57.7	51.6	52.3	34.5
Methylene Bridge Index	23.7	28.6	24.4	46.2

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Phenolic Resin Chemistry

EXPERIMENTAL PREPREG DATA SUMMARY

NMR, FT-IR, DMTA, and STANDARD TESTS document resin advancement in prepreg as time/temperature exposure increases.

STANDARD TESTS: Flow and drape decrease.

DMTA: **Bending $\tan \delta$** maximum moves to higher temperature.
Bending E'' maximum also moves to higher temperature.

NMR: Methylol Index decreases.
Methylene Bridge Index increases.

FT-IR: 1024/1000 ratio increases.
828/1000 ratio increases.

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Phenolic Resin Chemistry

CONCLUSIONS

Nmr is a valuable research tool for studying phenolic resin chemistry.

- Provides detailed structural information on phenolic resins.
- Provides quantitative information on resin advancement.
- Provides detailed information on resin composition (solvent level, formaldehyde to phenol ratio, etc.).

FT-IR is a convenient tool for assessing phenolic resin chemistry.

- Provides a rapid check on compositional integrity of phenolic resins.
- Can be used to follow resin aging.

Viscosity is a convenient measure of resin advancement.

- Compositional differences need to be accounted for.

DMTA is a useful technique for assessing prepreg viscoelastic properties.

Phenolic resin composition is controlled by raw materials and processing conditions. Resin advancement follows a finite reaction pathway.

